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A STUDY OF THE CONDUCTIVITY OF CERTAIN SALTS IN WATER, METHYL, ETHYL, AND PROPYL ALCOHOLS, AND IN MIXTURES OF THESE SOLVENTS.[1]

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INTRODUCTION.

Ever since the birth of the Arrhenius theory of electrolytic dissociation and the perfection of the Kohlrausch method for the measurement of the conductivity of solutions, the determination of the dissociation of electrolytes in aqueous solution has been the subject of extensive investigation. The work, however, has been almost exclusively confined to aqueous solutions, due to the fact that water is a solvent for so many substances, that it is a very good dissociant, and that it can readily be purified.

During the last few years, however, the measurement of dissociation has been extended, to a greater or less extent, to solutions in many solvents both inorganic and organic, and in some cases very interesting results have been obtained.

[1] From the dissertation of Charles F. Lindsay, submitted to the Board of University Studies in the Johns Hopkins University for the degree of Doctor of Philosophy.

The study of non-aqueous solutions has led to a comparison of the dissociating power of the various solvents, and this in turn has given rise to several generalizations attempting to connect dissociating power with other physical and chemical properties of solvents.

J. J. Thomson[1] and Nernst[2] have sought to connect the dissociating power of a solvent with its dielectric constant. Nernst says: "The greater the dielectric constant of a medium the greater becomes its electrolytic dissociation of dissolved substances under exactly similar conditions."

J. J. Thomson, after showing that molecules condensed on the surface of a conducting sphere will be completely dissociated, goes on to say: "The same effect would be produced by a substance possessing a very large specific inductive capacity. Since water is such a substance it follows, if we accept the view that the forces between the atoms are electrical in their origin, that when the molecules of a substance are in solution the forces between them are very much less than they are when the molecule is free and in the gaseous state."

Brühl[3] showed that while certain organic bodies as the oximes and the alcohols exist in a polymerized state in hydrocarbons, chloroform, or carbon bisulphide solution, the molecular complexes are more or less broken down in water solution, and to a less extent in alcohols, ethers, esters, ketones, and phenols. All of these also exert more or less dissociating power. According to his theory of the tetravalence of oxygen they are unsaturated compounds, and it is to this unsaturation that he ascribes dissociating power. He also attributes the dissociating power of solvents containing nitrogen to the fact that in these compounds nitrogen exists as a triad while it has the power of becoming pentavalent. He predicted dissociating power for compounds containing trivalent nitrogen, including the hydrazines, the amines, the diazo compounds, and liquid hydrocyanic acid, and even for other classes of unsaturated compounds as the trichlorides of

[1] Phil. Mag., **36**, 320.
[2] Ztschr. phys. Chem., **13**, 531.
[3] *Ibid.*, **18**, 514; **27**, 319; **30**, 1; Ber. d. chem. Ges., **28**, 2847, 2866; **30**, 163.

arsenic and phosphorus, the mercaptans, and alkyl sulphides. This prophecy is borne out, to some extent at least, by the later work of Walden. In his last paper Brühl has sought rather to connect dissociating power with a high dielectric constant, and with the tautomerizing power of the solvent.

Ciamician[1] concluded that dissociating power is a function of the chemical properties of the substance, and that those substances which resemble water chemically, as methyl and ethyl alcohol, should have the greatest dissociating power.

Konowalow,[2] from a study of the conductivity of the compounds which amines form with acids, holds that only those solutions conduct in which there is chemical action between the solvent and the dissolved substance.

Dutoit and Aston[3] advanced the idea that dissociating power is related to the amount of the polymerization of the solvent. Water and the alcohols which are good dissociants are also polymerized molecules, as shown by the surface-tension method of Ramsay and Shields.[4]

For further views on this subject consult the paper by Crompton.[5]

Donnan[6] says: "In a solution in which the solute is more or less ionized, one might suppose the ions to be surrounded by clusters of solvent molecules which had, so to speak, condensed around them, and opposed an obstacle to their recombination. Now one might suppose this state of things as being caused by some sort of specific attraction between the solvent molecules and electricity, *i. e.*, the electrons or electrical charges which are associated with the ions. Were this the case, one might expect this specific attraction to manifest itself in other ways. For example, if electrical nuclei were present in, or were produced by any means in air which was saturated with the vapor of an ionizing liquid, then it would be just possible that the specific attraction referred to above

[1] Ztschr. phys. Chem., **6**, 403.

[2] Wied. Ann., **49**, 733.

[3] Compt. rend., **125**, 240. See also Dutoit and Friderich: Bull. Soc. Chim., [3], **19**, 321.

[4] Ztschr. phys. Chem., **12**, 433.
J. Chem. Soc., **71**, 925.
Phil. Mag., [6], **15**, 305.

might help to produce condensation of the vapor around these nuclei under suitable conditions, *i. e.*, if the vapor were supersaturated by a sudden adiabatic expansion. If the liquid in question did not act as an ionizing solvent, it would be natural to expect that the condensation just alluded to would only occur when the vapor entered the really unstable (labile) region, or at any rate would only be produced by a much higher degree of supersaturation." From his experiments, however, he does not feel warranted in drawing any final conclusion.

PART I.

HISTORICAL SKETCH.

A review of the work done on the dissociating power of different solvents has recently been published by one of us in this JOURNAL.[1] Brief reference is given below to work carried out subsequent to the review in question.

Water has always been regarded as the best dissociant, but within the last few months another solvent, liquid hydrocyanic acid, has been found to produce greater dissociation.

Hydrocyanic Acid.—Schlundt[2] has measured the dielectric constant of liquid hydrocyanic acid and found the very large value of 95 at 21°, a value which exceeds that of water, which is 80 at the same temperature. It was, therefore, important, as bearing on the Nernst-Thomson theory of dissociation, that measurements of the conductivity of solutions in this solvent be made. This has been done by Centnerszwer[3] with the result that not only do solutions in hydrocyanic acid show greater conductivity, but the dissociation is also greater than in water. The substances worked with were potassium iodide and trimethylsulphonium iodide. Their conductivity at 0° was nearly the same as the conductivity of aqueous hydrochloric acid at 25°.

Sulphur Dioxide.—Walden and Centnerszwer[4] have very recently published the results of an extensive investigation on

[1] Jones: This JOURNAL, **25**, 232.
[2] J. Phys. Chem., **5**, 157.
[3] J. Russ. phys. chem. Soc., **33**, 545–549; Ztschr. phys. Chem., **39**, 217.
[4] Jones: Ztschr. phys. Chem., **39**, 513.

sulphur dioxide as a solvent. This is an extension of the older work of Walden.[1] They investigated the conductivity of nineteen salts, consisting of iodides, bromides, chlorides, and sulphocyanates of inorganic and organic bases. They show, first, that while in aqueous solution the molecular conductivities at 25° of monobasic halogen salts generally lie between 100 and 140, the corresponding values in sulphur dioxide vary between 3 and 157; second, that Kohlrausch's law of the independent migration velocities of the ions does not hold for solutions in sulphur dioxide. They have also shown by a series of conductivity measurements at different temperatures between —78° and 157° (the freezing-point and critical temperature of sulphur dioxide) that the molecular conductivity at first increases with the temperature, passes through a maximum, and then diminishes as the critical temperature is approached. This is seen at once to be just what would be expected from the polymerized solvent theory of Dutoit and Aston. As the temperature rises the association of the solvent decreases, and this would be expected to diminish the ionizing power. They have also determined the molecular weights of a number of electrolytes (salts) in liquid sulphur dioxide by the boiling-point method, reaching the remarkable result that many of these salts show a molecular weight greater than normal, or what is the same thing, the value of the van't Hoff coefficient "i" is less than unity. This they endeavor to show is due to the fact that, in addition to the electrolytic dissociation, an association takes place in the sulphur dioxide solutions. Facts similar to the maximum value in the temperature-conductivity curve, and to the abnormal values of the van't Hoff coefficient "i" were noticed by Franklin and Kraus[2] in their work on liquid ammonia.

The remaining work on inorganic solvents we owe chiefly to Walden.[3] He has investigated the solvent and ionizing power of the following compounds: Phosphorus trichloride, phosphorus tribromide, phosphorus oxychloride, arsenic trichloride, antimony trichloride, antimony pentachloride, boron

[1] Ber. d. chem. Ges., **32**, 2862.
[2] This JOURNAL, **20**, 836; **24**, 83.
[3] Ztschr. anorg. Chem., **25**, 209; **29**, 371.

trichloride, silicon tetrachloride, tin tetrachloride, sulphur monochloride, sulphuryl chloride, thionyl chloride, sulphur trioxide, and liquid bromine. Of these, sulphur monochloride, sulphuryl chloride, thionyl chloride, phosphorus oxychloride, arsenic trichloride, and antimony trichloride show considerable ionizing power, while solutions in the remaining solvents exhibit only the very slightest conductivity. In his next paper Walden adds a study of arsenic tribromide, chlorsulphuric acid, sulphuric acid, and the dimethyl ester of sulphuric acid. All of these show a strong tendency to ionize dissolved electrolytes. It is important to notice from this work of Walden that there appears to be no connection between dissociating power and chemical constitution. Antimony pentachloride does not dissociate electrolytes, while the trichloride dissociates to a very considerable extent. On the other hand, phosphorus trichloride does not dissociate, while phosphorus oxychloride does. It is thus evident that among the inorganic solvents, at least, a knowledge of the dissociating power of one solvent tells us nothing as to the dissociating power of substances closely related chemically.

Of the remaining work little need be said. Oddo[1] has also shown that phosphorus oxychloride strongly ionizes electrolytes. Tolloczko,[2] as well as Gareili and Bassani,[3] have worked with the halides of arsenic and antimony, showing them to have ionizing power. Kahlenberg and Lincoln[4] studied solutions of ferric chloride, antimony trichloride, bismuth trichloride, and mercuric chloride in phosphorus trichloride and arsenic trichloride, with results which confirm those mentioned above. Centnerszwer[5] is authority for placing cyanogen among the solvents which do not dissociate. Frankland and Farmer[6] have also shown that nitrogen peroxide does not dissociate, while Skilling[7] has shown that solutions in hydrogen sulphide show no conductivity.

The following table of inorganic solvents is given to show

[1] Atti R. Accad. dei Lincei Roma, [5], **10**, 452.
[2] Ztschr. phys. Chem., **30**, 705.
[3] Atti R. Accad. dei Lincei Roma, [5], **10**, 255.
[4] J. Phys. Chem., **3**, 12.
[5] Ztschr. phys. Chem., **39**, 217.
[6] J. Chem. Soc., **79**, 1356.
[7] This JOURNAL, **26**, 383.

what relations exist between dissociating power, dielectric constants, and the association factor :

Inorganic Solvents Which Effect Dissociation.

Solvent.	Dielectric constant.	Association factor.	Considered as
Hydrocyanic acid	95	?	saturated
Water	81.12	3.7	"
Ammonia	16.2	1.0	unsaturated
Sulphur dioxide	13.75	1.0	"
Nitric acid	?	1.7–1.9	saturated
Arsenic trichloride	12.35	?	unsaturated
Arsenic tribromide	?	?	"
Phosphorus oxychloride	13.9	1.00	saturated
Antimony trichloride	33.2	?	unsaturated
Thionyl chloride	9.05	1.08	"
Sulphuryl chloride	9.15	0.97	saturated
Dimethyl sulphate	?	?	"
Chlorsulphuric acid	?	?	"
Sulphuric acid	?	32.0	"
Sulphur monochloride	4.8	0.95–1.05	unsaturated

Inorganic Solvents Which Do Not Dissociate Electrolytes.

Bromine	3.18	1.2–1.3	saturated
Cyanogen	2.52	?	"
Sulphur trioxide	3.56		"
Boron trichloride	?	?	"
Phosphorus trichloride	3.36	1.02	unsaturated
Phosphorus tribromide	?	?	"
Antimony pentachloride	3.78	?	saturated
Silicon tetrachloride	?	1.06	"
Tin tetrachloride	3.2	?	"
Hydrogen sulphide	?	?	"
Nitrogen peroxide	?	?	"

The values for the association factors are taken from the researches of Ramsay and Shields[1] and Ramsay and Aston,[2] while those for the dielectric constants are almost wholly taken from the work of Turner.[3]

Mixed Solvents.

Hydrogen Dioxide and Water.—The dielectric constant of a

[1] Ztschr. phys. Chem., **12**, 433.
[2] J. Chem. Soc., **65**, 167.
[3] J. Phys. Chem., **8**, 503.

mixture of hydrogen dioxide and water is greater than that of pure water. This has been shown by Calvert,[1] and would lead one to suspect that electrolytes dissolved in such mixtures would have a greater conductivity than in pure water, in accordance with the Thomson-Nernst rule. The dissociating power of such mixtures has, however, not yet been determined. Reference should also be made to the later work of Calvert,[2] showing that hydrogen dioxide has acid properties, and to the work of Jones, Barnes, and Hyde[3] along the same lines.

Mixtures of Water and the Alcohols.—Only brief mention need be made of the work of Lenz,[4] Kerler,[5] Stephan,[6] Kablukoff,[7] Carrara,[8] Schall,[9] and Arrhenius.[10] Wakeman,[11] in quite an elaborate investigation, measured the conductivity of organic acids in mixtures of ethyl alcohol and water in varying proportions. The results show that the conductivity becomes gradually smaller as the amount of alcohol becomes larger and larger. This is just what would be expected from the relative conductivities in these two solvents.

Zelinsky and Krapiwin[12] have, however, obtained results of a very different character. They found that the salts with which they worked, when dissolved in a mixture of methyl alcohol and water containing 50 per cent methyl alcohol, gave a conductivity considerably less than the conductivity in either alcohol or water.

Similar results were obtained by Cohen[13] with ethyl alcohol and water, but only when the mixture contained very little water, and at dilutions which were quite large, as is shown by the following table:

[1] Ann. der Phys., **1**, 483.
[2] Ztschr. phys. Chem., **38**, 513.
[3] This JOURNAL, **27**, 22.
[4] Mem. de l'Acad. de St. Petersbourg, [7], **30**, 1881.
[5] Dissertation (Erlangen), 1884.
[6] Wied. Ann., **17**, 673.
[7] Ztschr. phys. Chem., **1**, 432.
[8] Gazz. chim. ital., **16**, 1.
[9] Ztschr. phys. Chem., **14**, 701.
[10] *Ibid.*, **9**, 487.
[11] *Ibid.*, **11**, 49.
[12] *Ibid.*, **21**, 35.
[13] *Ibid.*, **25**, 31.

Potassium Iodide.

	Pure alcohol.	80 per cent alcohol.
v.	μ_v 18°.	μ_v 18°.
64	26.1	30.9
128	29.2	32.2
256	31.8	33.2
512	34.4	34.1
1024	36.0	34.5
2048	36.3	35.0

From an examination of the above results it is seen that the conductivities in the mixtures of water and alcohol are the greater until a dilution of 512 liters is reached. At greater dilutions the conductivity in the pure alcohol becomes greater than that of the alcohol containing 20 per cent of water.

In general, however, Cohen found that addition of water increased the conductivity, as we would expect.

PART II.

EXPERIMENTAL.

This work was undertaken as an extension of the older work of Zelinsky and Krapiwin,[1] and Cohen,[2] on the conductivity of electrolytes in mixtures of methyl and ethyl alcohol with water. Zelinsky and Krapiwin, in their work, have shown that solutions in a 50 per cent mixture of methyl alcohol and water have a much less conductivity than in the pure alcohol itself. They have also shown that the slightest addition of water to a solution of an electrolyte in absolute methyl alcohol produced a lowering of its conducting power.

We have extended this work by making conductivity measurements of solutions in which the solvents have been mixtures of methyl alcohol and water of varying composition. By this means we have been able to plot curves showing for each salt with which we have worked, the mixture of methyl alcohol and water having the least dissociating power.

We have also worked with ethyl alcohol, propyl alcohol, and with mixtures of ethyl alcohol and water, propyl alcohol and water, and of methyl and ethyl alcohols.

[1] *Loc. cit.*
[2] *Loc. cit.*

The work has, for the most part, been done both at 0° and 25°. In this way we have been able to calculate the temperature coefficients of conductivity of the various salts in the different solvents and, what is of more importance, to show the influence of temperature on the minimum values mentioned above.

The salts used are potassium iodide, strontium iodide, ammonium bromide, cadmium bromide, ferric chloride, and lithium nitrate.

Apparatus.

In all this work the Kohlrausch method of measuring conductivity was employed. The bridge wire used was a meter in length and made of "manganin." The resistance coils

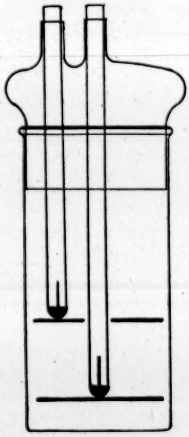


Fig. I.

were manufactured by Leeds & Co., of Philadelphia, and were guaranteed accurate to 1/25 of 1 per cent.

The cells used were of the following form (Fig. I.), the difference between them and the ordinary Arrhenius cell being that they are provided with a ground-glass top to

prevent evaporation of the more volatile solvents, and to protect the anhydrous alcohols from the moisture of the baths and air. In some cases the ground-glass joint was also covered with paraffin as an extra precaution.

The glass tubes carrying the electrodes were shoved through thin rubber tubes, and then inserted into the glass tubes in the cap. Sealing wax was then run over the outside of the joint.

The zero-bath was prepared as follows: A large glass battery-jar was filled with pure, finely crushed ice, and moistened with distilled water. This was placed in a water-bath, the space between the two being filled with finely crushed ice. By this means it was possible to keep a cell within $0°.02$ of zero for hours. The $25°$ bath was of the ordinary form and was stirred by means of a small hot-air engine.

The thermometers used were graduated to $0°.04$ and were carefully calibrated. The burettes and flasks were also carefully calibrated.

Solvents.

Water.—All the water used in this work was purified as follows: Ordinary distilled water was first distilled from acidified potassium bichromate. This water was redistilled from potassium bichromate acidified with sulphuric acid, and then from barium hydroxide. The water purified in this way has a conductivity of never more than 2×10^{-6} and sometimes as low as 0.8×10^{-6}.

Methyl Alcohol.—The methyl alcohol used was the best commercial article which could be obtained. It was first boiled with calcium oxide, then distilled and allowed to stand over anhydrous copper sulphate for weeks. Before use it was distilled from the copper sulphate and then from sodium. None of the alcohol used in making up the absolute alcohol solutions had been distilled from sodium more than twenty-four hours before use. It had a conductivity of about 2.3×10^{-6}.

Ethyl Alcohol.—The ethyl alcohol was the best obtainable article and was purified in the same manner as the methyl alcohol. Its conductivity had a mean value of 2×10^{-7}.

Propyl Alcohol.—The propyl alcohol was Kahlbaum's best,

and before use was distilled from anhydrous copper sulphate and sodium. It had a conductivity of 0.8×10^{-7}.

Solutions.

The method of making up the original mother-solutions will be given when the various electrolytes are considered.

From this mother solution the remaining solutions were made by successive dilutions by means of burettes and measuring-flasks. In the cases where this would necessitate the use of small quantities of the solution a second mother-solution was made, and from this successive dilutions were prepared.

In preparing the solutions in the mixed solvents a sufficient quantity of the solvent was made by mixing the constituents in the required proportions. This was then used in the same manner as a simple solvent.

In preparing these mixed solvents the following method was used: "x" cc. of an alcohol were diluted to 100 cc. In the following discussion such a solution would be designated as — alcohol x per cent. In making mixtures of methyl alcohol and ethyl alcohol, the methyl alcohol was measured and diluted with the ethyl alcohol, and the concentration expressed in terms of the methyl alcohol.

Conductivity Measurements.

In all determinations of conductivity from three to five different resistances were used, and the values given in the tables are the mean of these values.

Potassium Iodide.

The salt used in this work was recrystallized a number of times. It was then carefully dried and kept in a desiccator. All the mother-solutions were made by direct weighing.

Table 1.—Molecular Conductivity of Potassium Iodide in Water.

Potassium iodide, KI. Molecular weight, 166.00.

v.	μ_v 0°.	μ_v 25°.
64	74.09	132.1
128	76.4 D	135.4
256	77.01	138.0
512	78.0 D	139.6
1024	77.96	140.7

The values of the conductivity at 0° marked "D" were obtained by Jones and Douglas,[1] while those at 25° are taken from the work of Ostwald.

Table II.—Molecular Conductivity of Potassium Iodide in Ethyl Alcohol.

v.	μ_v 0°.	μ_v 25°.
64	19.12	29.40
128	21.36	33.02
256	22.66	36.02
512	25.00	38.63
1024	27.43	41.35

Table III.—Molecular Conductivity of Potassium Iodide in Methyl Alcohol.

v.	μ_v 0°.	μ_v 25°.
64	59.32	82.87
128	63.88	88.49
256	67.73	93.73
512	69.85	98.36
1024	71.23	102.0

The conductivity of solutions of potassium iodide in methyl alcohol had already been determined by both Zelinsky and Krapiwin,[2] and Carrara,[3] but with such different results that the above measurements seemed necessary. Our measurements agree very well with those of Zelinsky and Krapiwin, as is seen from the following table:

Table IV.—Molecular Conductivity of Potassium Iodide in Methyl Alcohol.

v.	μ_v 25°. Carrara.	μ_v 25°. Zelinsky and Krapiwin.
64	78.7	82.52
128	84.7	88.69
256	88.2	93.85
512	90.8	98.19
1024	93.0	102.2

[1] This JOURNAL, **26**, 428.
[2] Ztschr. phys. Chem., **21**, 35.
[3] Gazz. chim. ital., **26**, (1), 119.

Table V.—Molecular Conductivity of Potassium Iodide in Methyl Alcohol (20 Per Cent) and Water.

v.	μ_v 0°.	μ_v 25°.
64	45.69	91.91
128	47.26	93.78
256	47.79	95.64
512	48.45	97.12
1024	49.07	98.10

Table VI.—Molecular Conductivity of Potassium Iodide in Methyl Alcohol (40 Per Cent) and Water.

v.	μ_v 0°.	μ_v 25°.
64	35.48	72.14
128	35.92	73.69
256	36.52	75.14
512	37.02	76.25
1024	37.85	77.68

Table VII.—Molecular Conductivity of Potassium Iodide in Methyl Alcohol (50 Per Cent) and Water.

v.	μ_v 0°.	μ_v 25°.
64	33.73	67.46
128	34.44	68.79
256	35.13	70.37
512	36.05	71.72
1024	36.76	72.57

Table VIII.—Molecular Conductivity of Potassium Iodide in Methyl Alcohol (65 Per Cent) and Water.

v.	μ_v 0°.	μ_v 25°.
64	35.12	65.04
128	35.71	67.25
256	36.49	68.78
512	37.23	70.00
1024	37.75	70.94

Table IX.—Molecular Conductivity of Potassium Iodide in Methyl Alcohol (80 Per Cent) and Water.

v.	μ_v 0°.	μ_v 25°.
64	39.03	67.78
128	40.51	70.33
256	41.83	71.83
512	43.23	73.16
1024	44.45	74.81

Table X.—Molecular Conductivity of Potassium Iodide in Ethyl Alcohol (50 Per Cent) and Water.

v.	μ_v 0°.	μ_v 25°.
64	19.26	48.30
128	19.82	50.07
256	20.35	50.80
512	20.92	51.97
1024	21.43	52.52

Table XI.—The Molecular Conductivity of Potassium Iodide, Methyl Alcohol (50 Per Cent) and Ethyl Alcohol.

v.	μ_v 0°.	μ_v 25°.
64	36.74	54.18
128	39.46	58.52
256	41.93	62.13
512	44.46	65.93
1024	46.89	69.61

Table XII.—Temperature Coefficients of Conductivity of Potassium Iodide in Water (0°–25°).

v.	Temperature coefficient.
64	2.26
128	2.30
256	2.35
512	2.40
1024	2.52

Table XIII.—Temperature Coefficients of Conductivity of Potassium Iodide in Methyl Alcohol (0°–25°).

v.	Temperature coefficient.
64	0.942
128	0.984
256	1.04
512	1.14
1024	1.23

Table XIV.—Temperature Coefficients of Conductivity of Potassium Iodide in Ethyl Alcohol (0°–25°).

v.	Temperature coefficient.
64	0.411
128	0.466
256	0.534
512	0.545
1024	0.557

Table XV.—Temperature Coefficients of Conductivity of Potassium Iodide in Mixtures of Methyl Alcohol and Water of Various Compositions.

v.	20 per cent.	40 per cent.	50 per cent.	65 per cent.	80 per cent.
64	1.83	1.47	1.35	1.17	1.15
128	1.86	1.51	1.37	1.26	1.17
256	1.91	1.54	1.41	1.29	1.20
512	1.95	1.57	1.43	1.31	1.20
1024	1.96	1.59	1.43	1.32	1.21

Table XVI.—Temperature Coefficients of Conductivity of Potassium Iodide in a 50 Per Cent Mixture of Ethyl Alcohol and Water (0°–25°).

v.	Temperature coefficient.
64	1.16
128	1.25
256	1.22
512	1.24
1024	1.24

Table XVII.—Temperature Coefficients of Conductivity of Potassium Iodide in a 50 Per Cent Mixture of Methyl and Ethyl Alcohols (0°–25°).

v.	Temperature coefficient.
64	0.698
128	0.762
256	0.808
512	0.859
1024	0.909

In order to see the connection existing between the conducting power of the solutions in the various solvents, the following tables are given for the sake of comparison :

Table XVIII.—Comparison of the Molecular Conductivity of Potassium Iodide in Water, Methyl Alcohol, and Mixtures of these Solvents at 0°.

v.	0 per cent.	20 per cent.	40 per cent.	50 per cent.	65 per cent.	80 per cent.	100 per cent.
64	74.09	....	35.48	33.73	35.12	39.03	59.32
128	76.4 D	47.26	35.92	34.44	35.71	40.51	63.88
256	77.01	47.79	36.52	35.13	36.49	41.83	67.73
512	78.0 D	48.45	37.02	36.05	37.23	43.23	69.85
1024	77.96	49.07	37.85	36.76	37.75	44.45	71.23

The values in this table are plotted in Fig. II. It is seen that the values of the molecular conductivity reach a mini-

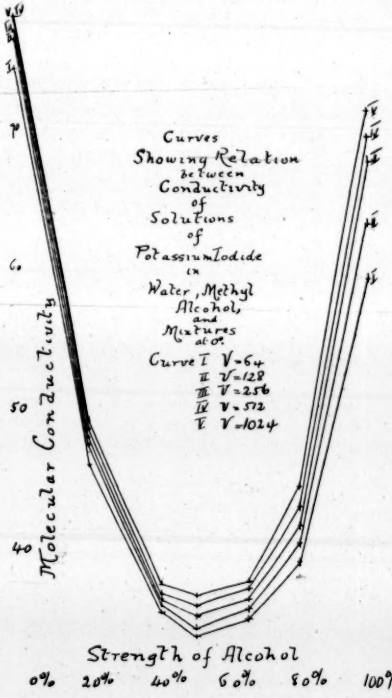


Fig. II.

mum in a mixture of methyl alcohol and water containing 50 per cent methyl alcohol.

It is also seen that an addition of approximately 10 per cent of alcohol lowers the conductivity of the water solutions to that of an alcoholic solution.

Table XIX.—Comparison of the Molecular Conductivity of Potassium Iodide in Water, Methyl Alcohol, and Mixtures of these Solvents, at 25°.

V.	0 per cent.	20 per cent.	40 per cent.	50 per cent.	65 per cent.	80 per cent.	100 per cent.
64	132.1	91.91	72.14	67.46	65.04	67.78	82.87
128	135.4	93.78	73.69	68.79	67.25	70.33	88.49
256	138.0	95.64	75.14	70.37	68.78	71.83	93.73
512	139.6	97.12	76.25	71.72	70.00	73.16	98.36
1024	140.7	98.10	77.68	72.57	70.94	74.81	102.0

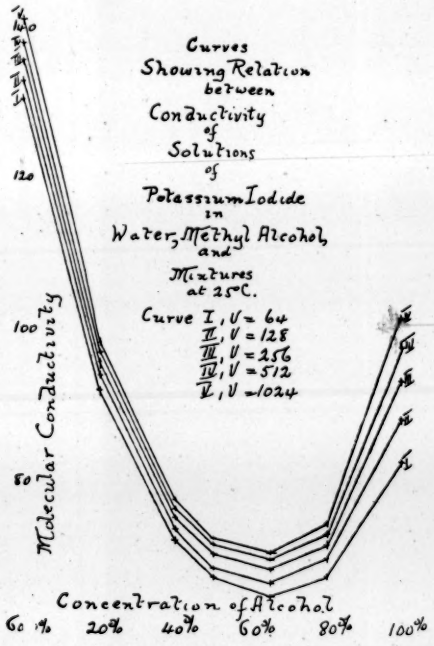


Fig. III.

The results given in this table are plotted in Fig. III. The curves are of the same general form as the preceding. The chief points of difference are: (1) The minimum point has shifted to the right, corresponding now to an alcohol-water mixture of about 65 per cent. The increase to the right of the minimum is much less rapid than that to the left, the difference being due to the fact that the temperature coefficient of conductivity is much greater in water than in methyl alcohol. The alcohol-water mixture having the same conducting power as the solution in pure methyl alcohol has also changed. In this case it changes from an alcohol of about 19 per cent to an alcohol of about 30 per cent, depending upon the concentration of the solution.

Table XX.—Comparison of the Molecular Conductivity of Potassium Iodide in Methyl Alcohol, Water, and a 50 Per Cent Mixture of these Solvents at 0°.

	Water.	Mixture.	Ethyl alcohol.
$v.$	$\mu_v.$	$\mu_v.$	$\mu_v.$
64	74.09	19.26	19.12
128	76.4	19.82	21.36
256	77.01	20.35	22.66
512	78.0	20.92	25.00
1024	77.96	21.43	27.43

Table XXI.—Comparison of the Molecular Conductivity of Potassium Iodide in Methyl Alcohol, Water, and a 50 Per Cent Mixture of these Solvents at 25°.

	Water.	Mixture.	Ethyl alcohol.
$v.$	$\mu_v.$	$\mu_v.$	$\mu_v.$
64	132.1	48.30	29.40
128	135.4	50.07	33.02
256	138.0	50.80	36.02
512	139.6	51.97	38.63
1024	140.7	52.52	41.35

Cohen[1] has shown that solutions of potassium iodide in a mixture of alcohol and water show a minimum in the conductivity, but only at great dilutions (512), and when the amount of water present is small. His work, however, was all done at 18° C. From the results in Table XX. we see that at 0°

[1] Ztschr. phys. Chem., **25**, 31.

we have a minimum in the conductivity values for an alcohol as dilute as 50 per cent, and in solutions which are comparatively strong, namely from $v = 128$. In all probability in alcohol of 75 to 80 per cent a much greater depression would be found. This is, however, a subject for future investigation. At 25° all trace of a minimum has disappeared.

Table XXII.—Comparison of the Molecular Conductivity of Potassium Iodide in Methyl Alcohol, Ethyl Alcohol, and a 50 Per Cent Mixture of these Solvents at 0°.

	Methyl alcohol.	Mixture.	Ethyl alcohol.
v.	μ_v.	μ_v.	μ_v.
64	59.32	36.74	19.12
128	63.88	39.46	21.36
256	67.73	41.93	22.66
512	69.85	44.46	25.00
1024	71.23	46.89	27.43

Table XXIII.—Comparison of the Molecular Conductivity of Potassium Iodide in Methyl Alcohol, Ethyl Alcohol, and a 50 Per Cent Mixture of these Solvents at 25°.

	Methyl alcohol.	Mixture.	Ethyl alcohol.
v.	μ_v.	μ_v.	μ_v.
64	82.87	54.18	29.40
128	88.49	58.52	33.02
256	93.73	62.13	36.02
512	98.36	65.93	38.63
1024	102.0	69.61	41.35

The last two tables make it clear that in a mixture of methyl and ethyl alcohols, the conductivity of potassium iodide shows no minimum value when compared with the conductivity in the pure solvents. In fact, the conductivity values for the solutions in the mixed solvent approach the mean value of the conductivities in the pure solvents. Thus, at 0° the observed value of the conductivity in the mixture, for $v = 64$, is 36.74, while the mean of the conductivities at the same dilution in the pure solvents is 39.22. In all cases, however, the conductivity in the mixture lies below this mean value.

Ammonium Bromide.

The salt used in this work was carefully recrystallized, and on sublimation left no residue. It was thoroughly dried and kept in a desiccator. All the mother solutions were made by direct weighing.

Table XXIV.—Molecular Conductivity of Ammonium Bromide in Water.

Ammonium bromide, NH_4Br. Molecular weight, 98.04.

v.	μ_v 0°.	μ_v 25°.
64	74.22	135.3
128	75.23	138.6
256	76.62	141.2
512	77.49	143.5
1028	77.78	145.6

Table XXV.—Molecular Conductivity of Ammonium Bromide in Methyl Alcohol.

v.	μ_v 0°.	μ_v 25°.
64	58.71	79.56
128	63.16	85.80
256	66.45	90.88
512	68.51	94.99
1024	70.40	98.24

The values at 25° in these two tables are all taken from the work of Zelinsky and Krapiwin.

Table XXVI.—Molecular Conductivity of Ammonium Bromide in Ethyl Alcohol.

v.	μ_v 0°.
64	16.71
128	18.83
256	19.66
512	22.66
1024	22.88

Table XXVII.—Molecular Conductivity of Ammonium Bromide in Methyl Alcohol (50 Per Cent) and Water.

v.	μ_v 0°.
64	34.85
128	35.78
256	36.36
512	37.11
1024	37.49

Table XXVIII.—Molecular Conductivity of Ammonium Bromide in Ethyl Alcohol (50 Per Cent) and Water.

v.	μ_v 0°.
64	19.42
128	19.89
256	20.09
512	20.70
1024	21.50

Table XXIX.—Molecular Conductivity of Ammonium Bromide in Methyl Alcohol (50 Per Cent) and Ethyl Alcohol.

v.	$-\mu_v$ 0°.
64	34.15
128	38.40
256	39.75
512	41.06
1024	42.00

Table XXX.—Temperature Coefficients of Conductivity of Ammonium Bromide in Water (0°–25°).

v.	Temperature coefficient.
64	2.44
128	2.54
256	2.58
512	2.64
1024	2.71

Table XXXI.—Temperature Coefficients of Conductivity of Ammonium Bromide in Methyl Alcohol (0°–25°).

v.	Temperature coefficient.
64	0.834
128	0.906
256	0.977
512	1.059
1024	1.114

Table XXXII.—Comparison of the Molecular Conductivity of Ammonium Bromide in Water, Methyl Alcohol, and a 50 Per Cent Mixture of these Solvents at 0°.

v.	Water. μ_v 0°	Mixture. μ_v 0°.	Methyl alcohol. μ_v 0°.
64	74.32	34.85	58.71
128	75.23	35.78	63.16
256	76.62	36.36	66.45
512	77.49	37.11	68.51
1024	77.78	37.49	70.40

Table XXXIII.—Molecular Conductivity of Ammonium Bromide ($v = 64$) in Methyl Alcohol, Water, and Mixtures of These Solvents at 0°.

Alcohol. Per cent.	μ_v 0°.
0	74.22
20	47.96
50	34.85
65	34.68
80	40.55
100	58.71

We see that in these results we have practically the same phenomenon as in the case of potassium iodide. In the case of ammonium bromide the minimum point in the conductivity values appears to be reached with an alcohol of 50 per cent.

Table XXXIV.—Comparison of the Molecular Conductivity of Ammonium Bromide in Water, Ethyl Alcohol, and a 50 Per Cent Mixture of These Solvents at 0°.

	Water.	Mixture.	Ethyl alcohol.
v.	μ_v 0°.	μ_v 0°.	μ_v 0°.
64	74.22	19.42	16.71
128	75.23	19.89	18.83
256	76.62	20.09	19.66
512	77.49	20.70	22.66
1024	....	21.50	22.88

From this table we see that here also a 50 per cent ethyl alcohol gives a minimum, but only in the case of the more dilute solutions, namely for dilutions $v = 512$ and 1024.

Table XXXV.—Comparison of the Molecular Conductivity of Ammonium Bromide in Methyl Alcohol, Ethyl Alcohol, and a 50 Per Cent Mixture of these Solvents at 0°.

	Methyl alcohol.	Mixture.	Ethyl alcohol.
v.	μ_v 0°.	μ_v 0°.	μ_v 0°.
64	58.71	34.15	16.71
128	63.16	38.40	18.83
256	66.45	39.75	19.66
512	68.51	41.06	22.66
1024	70.40	42.00	22.88

In this comparison there is no trace of a minimum, nor does there appear to be the slightest chance of there being one for any mixture of methyl and ethyl alcohols.

Strontium Iodide.

The strontium iodide used in this work was a sample of Bender and Hobein's best material. It was practically free from impurities. The material was dried as follows: It was carefully heated with a little ammonium iodide in a current of pure, dry hydrogen until all the water and ammonium iodide had been driven off. After cooling in the stream of hydrogen it was at once dissolved. The solutions were perfectly neutral and showed not the slightest coloration with starch solution. No trace of ammonium salts could be detected. The solutions were preserved in the dark in tightly stoppered bottles.

Table XXXVI.—Molecular Conductivity of Strontium Iodide in Water.

Strontium iodide, SrI_2. Molecular weight, 341.3.

v.	μ_v 0°.	μ_v 25°.
32	113.1	205.3
64	117.7	214.5
128	122.1	223.1
256	126.0	231.8
512	129.8	240.2
1024	132.6	245.9

Table XXXVII.—Molecular Conductivity of Strontium Iodide in Methyl Alcohol.

v.	μ_v 0°.	μ_v 25°.
32	75.82	101.4
64	85.01	115.3
128	94.76	128 6
256	104.4	141.4
512	114.0	153.9
1024	123.4	166.3

Table XXXVIII.—Molecular Conductivity of Strontium Iodide in Ethyl Alcohol.

v.	μ_v 0°.	μ_v 25°.
32	17.44	24.00
64	20.28	28.88
128	23.66	33.53
256	27.00	38.88
512	32.07	46.13
1024	36.01	51.25

Table XXXIX.—Molecular Conductivity of Strontium Iodide in Propyl Alcohol.

v.	μ_v 0°.	μ_v 25°.
32	4.70	7.58
64	5.62	8.84
128	6.52	10.20
256	7.41	11.32

Table XL.—Molecular Conductivity of Strontium Iodide in Methyl Alcohol (25 Per Cent) and Water.

v.	μ_v 0°.	μ_v 25°.
32	63.06	131.3
64	66.05	138.5
128	68.62	145.3
256	70.98	152.3
512	73.10	157.4
1024	75.51	161.9

Table XLI.—Molecular Conductivity of Strontium Iodide in Methyl Alcohol (50 Per Cent) and Water.

v.	μ_v 0°.	μ_v 25°.
32	50.19	103.8
64	52.61	109.9
128	55.05	115.3
256	57.18	120.1
512	....	124.3
1024	61.03	128.5

Table XLII.—Molecular Conductivity of Strontium Iodide in Methyl Alcohol (75 Per Cent) and Water.

v.	μ_v 0°.	μ_v 25°.
32	55.53	98.09
64	59.24	104.8
128	62.85	111.4
256	66.68	118.0
512	69.98	124.8
1024	73.22	131.4

Table XLIII.—Molecular Conductivity of Strontium Iodide in Ethyl Alcohol (50 Per Cent) and Water.

v.	μ_v 0°.	μ_v 25°.
32	28.32	72.51
64	29.72	76.89
128	31.25	80.21
256	32.23	83.21
512	33.22	86.44
1024	34.16	89.32

Table XLIV.—Molecular Conductivity of Strontium Iodide in Propyl Alcohol (50 Per Cent) and Water.

v.	μ_v 0°.	μ_v 25°.
32	27.40	67.67
64	28.63	71.63
128	29.83	75.44
256	30.98	79.32

Table XLV.—Temperature Coefficients of Conductivity of Strontium Iodide in Water (0°–25°).

v.	Temperature coefficient.
32	3.29
64	3.87
128	4.04
256	4.23
512	4.42
1024	4.53

Table XLVI.—Temperature Coefficients of Conductivity of Strontium Iodide in Methyl Alcohol (0°–25°).

v.	Temperature coefficient.
32	1.02
64	1.21
128	1.35
256	1.48
512	1.60
1024	1.72

Table XLVII.—Temperature Coefficients of Conductivity of Strontium Iodide in Ethyl Alcohol (0°–25°).

v.	Temperature coefficient.
32	0.262
64	0.344
128	0.396
256	0.475
512	0.562
1024	0.610

Table XLVIII.—Temperature Coefficients of Conductivity of Strontium Iodide in Propyl Alcohol (0°–25°).

v.	Temperature coefficient.
32	0.115
64	0.129
128	0.147
256	0.156

Table XLIX.—Temperature Coefficients of Conductivity of Strontium Iodide in Various Mixtures of Methyl Alcohol and Water.

v.	25 per cent.	50 per cent.	75 per cent.
32	2.73	2.14	1.70
64	2.90	2.29	1.82
128	3.07	2.41	1.94
256	3.25	2.52	2.05
512	3.37	2.59	2.19
1024	3.45	2.70	2.33

Table L.—Temperature Coefficients of Conductivity of Strontium Iodide in Ethyl Alcohol (50 Per Cent) and Water (0°–25°).

v.	Temperature coefficient.
32	1.77
64	1.89
128	1.96
256	2.04
512	2.13
1024	2.21

Table LI.—Temperature Coefficients of Conductivity of Strontium Iodide in Propyl Alcohol (50 Per Cent) and Water (0°–25°).

v.	Temperature coefficient.
32	1.61
64	1.72
128	1.82
256	1.93

Table LII.—Comparison of the Molecular Conductivity of Strontium Iodide in Water, Methyl Alcohol, and Mixtures of these Solvents at 0°.

v.	0 per cent.	20 per cent.	50 per cent.	75 per cent.	100 per cent.
32	113.1	63.06	50.19	55.53	75.82
64	117.7	66.05	52.61	59.24	85.01
128	122.1	68.62	55.05	62.85	94.76
256	126.0	70.98	57.18	66.68	104.4
512	129.8	73.10	59.51	69.98	114.0
1024	132.6	75.51	61.03	73.22	123.4

The results of Table LII. are plotted in Fig. IV. It is

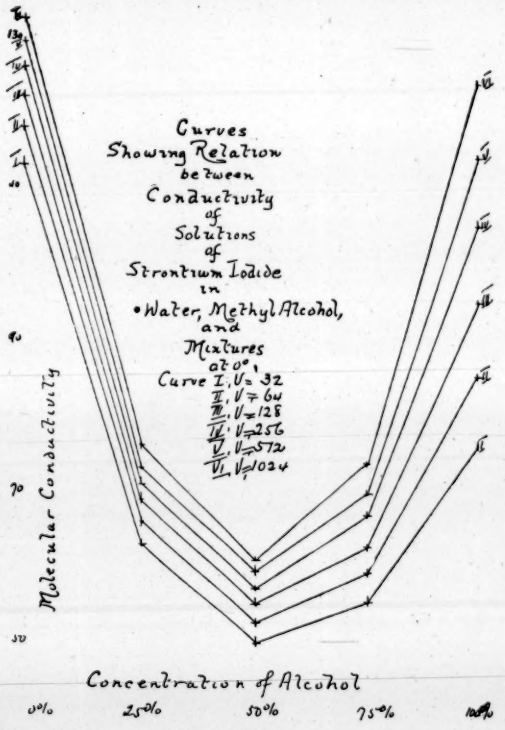


Fig IV.

seen that the curve is of identically the same form as that for potassium iodide at the same temperature. The minimum point is reached with an alcohol of about 50 per cent.

Table LIII.—Comparison of the Molecular Conductivity of Strontium Iodide in Water, Methyl Alcohol, and Mixtures of these Solvents at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
32	205.3	131.3	103.8	98.09	101.4
64	214.5	138.5	109.9	104.8	115.3
128	223.1	145.3	115.3	111.4	128.6
256	231.8	152.3	120.1	118.0	141.4
512	240.2	157.4	124.3	124.8	153.9
1024	245.9	161.9	128.5	131.4	166.3

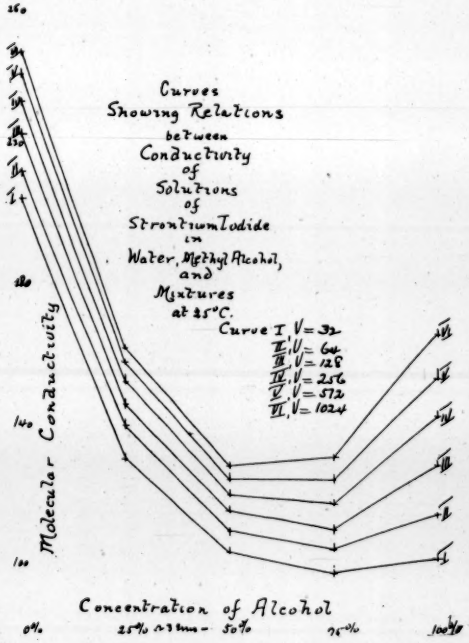


Fig. V.

The results of this table are plotted as Fig. V. It is seen that in this curve the effect of temperature has been such as to almost completely blot out the minimum value in the curve for $v = 32$; and in the other dilutions the minimum is much less pronounced than in the curves thus far studied. The effect of temperature is also to shift the minimum point to the right, the minimum point existing for an alcohol of about 65 to 70 per cent.

Table LIV.—Comparison of the Molecular Conductivity of Strontium Iodide in Water, Ethyl Alcohol, and a 50 Per Cent Mixture of these Solvents.

	Water.	Mixture.	Ethyl alcohol.
v.	μ_v.	μ_v.	μ_v.
	0°.		
32	113.1	28.32	17.44
64	117.7	29.72	20.28
128	122.1	31.25	23.66
256	126.0	32.23	27.00
512	129.8	33.22	32.07
1024	132.6	34.16	36.01
	25°.		
32	205.3	72.51	24.00
64	214.5	76.89	28.88
128	223.1	80.21	33.53
256	231.8	83.21	38.88
512	240.2	86.44	46.13
1024	245.9	89.32	51.25

In the table for 0° we see that the values for pure ethyl alcohol are, in the stronger solutions, much smaller than those for the mixture. They, however, increase more rapidly, and in the most dilute solutions pass the values for the mixture, giving us again the minimum point. At 25° there is not the slightest trace of a minimum point, although the values are well below the mean of the values for the pure solvents.

In comparing the values for a mixture of propyl alcohol and water with those for the pure solvents, we find that there is not the slightest trace of a minimum at either 0° or 25°.

Cadmium Iodide.

The cadmium iodide which was used was a sample which had been employed in some previous work in this laboratory, and had then been very carefully purified. The solutions were made by direct weighing.

Table LV.—Comparison of the Molecular Conductivity of Cadmium Iodide in Methyl Alcohol, Water, and a 50 Per Cent Mixture of these Solvents at 25°.

Cadmium iodide, CdI_2. Molecular weight, 366.1.

	Water.	Mixture.	Methyl alcohol.
v.	μ_v.	μ_v.	μ_v.
16	62.98	20.31	13.07
32	81.96	24.22	13.59
64	104.7	31.17	14.16
128	129.3	42.03	14.78
256	153.6	50.43	15.44

Table LVI.—Comparison of the Molecular Conductivity of Cadmium Iodide in Varying Mixtures of Methyl Alcohol and Water at 25°.

Concentration of alcohol.	$v = 16$.	$v = 64$.
Per cent.	μ_v.	μ_v.
0	62.98	104.7
50	20.31	31.17
60	....	25.66
80	14.70	18.41
100	13.07	14.16

When the results in the second part of this table are plotted as curves no trace of a minimum appears (Fig. VI.). A considerable difference is, however, noticed between the values obtained and those required from the law of mixtures, the conductivity values obtained being always lower.

Lithium Nitrate.

The lithium nitrate used in this work was a sample from Kahlbaum. It was dried in an air-bath at 150° and kept in a desiccator. The solutions were made by direct weighing.

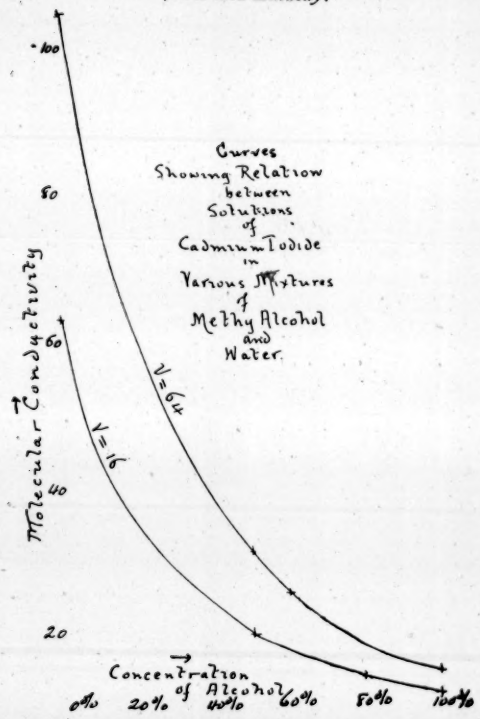


Fig. VI.

Table LVII.—Molecular Conductivity of Lithium Nitrate in Water.

Lithium nitrate, $LiNO_3$. Molecular weight, 69.0.

v.	μ_v 0°.	μ_v 25°.	μ_v 25°. (Ostwald.)
32	50.00	91.83	91.8
64	51.49	94.62	94.5
128	52.51	98.00	97.7
256	53.40	99.68	100.0
512	54.70	101.3	101.5
1024	55.30	102.3	102.0

Table LVIII.—Molecular Conductivity of Lithium Nitrate in Methyl Alcohol.

v.	μ_v 0°.	μ_v 25°.
32	45.97	63.51
64	50.12	69.32
128	53.95	74.51
256	56.67	80.57
512	60.06	83.31
1024	63.40	86.46

From these two tables we see that at 0° the conductivity in pure methyl alcohol, although starting lower than the conductivity in water, increases more rapidly, so that we have solutions in methyl alcohol with greater conductivity than solutions of the same strength in water. That our measurements are accurate is made more probable by the close agreement with Ostwald's values. The solutions measured at 0° were the same as at 25°. The conductivity of a number of the solutions in methyl alcohol was redetermined, using a different sample of an alcohol and salt. In all cases the agreement was all that could be desired.

Table LIX.—Molecular Conductivity of Lithium Nitrate in Ethyl Alcohol.

v.	μ_v 0°.	μ_v 25°.
32	14.29	21.99
64	15.60	24.85
128	17.52	27.72
256	19.39	30.84
512	21.36	33.25
1024	23.29	35.52

Table LX.—Molecular Conductivity of Lithium Nitrate in Ethyl Alcohol (50 Per Cent) and Water.

v.	μ_v 0°.	μ_v 25°.
32	13.10	33.73
64	13.56	35.57
128	14.27	37.08
256	14.63	38.85
512	15.45	40.14
1024	16.25	41.35

From Tables LVIII. and LIX. it is seen that with lithium nitrate a minimum point is found in the conductivity values at 0°, and through all the dilutions employed. At 25° no trace of minimum values is apparent.

Table LXI.—Molecular Conductivity of Lithium Nitrate in Methyl Alcohol (25 Per Cent) and Water.

v.	μ_v 0°.	μ_v 25°.
32	29.15	60.56
64	29.68	62.16
128	30.15	63.77
256	30.70	64.96
512	31.35	66.78
1024	32.56	69.02

Table LXII.—Molecular Conductivity of Lithium Nitrate in Methyl Alcohol (50 Per Cent) and Water.

v.	μ_v 0°.	μ_v 25°.
32	23.59	47.87
64	24.49	49.92
128	25.03	51.50
256	25.71	53.57
512	26.35	54.62
1024	27.35	55.60

Table LXIII.—Molecular Conductivity of Lithium Nitrate in Methyl Alcohol (75 Per Cent) and Water.

v.	μ_v 0°.	μ_v 25°.
32	26.67	47.06
64	27.95	49.52
128	28.66	51.64
256	29.51	54.36
512	30.64	56.68
1024	31.91	58.56

Table LXIV.—Temperature Coefficients of Conductivity of Lithium Nitrate in Water (0°–25°).

v.	Temperature coefficient.
32	1.67
64	1.72
128	1.82
256	1.85
512	1.86
1024	1.88

Table LXV.—Temperature Coefficients of Conductivity of Lithium Nitrate in Methyl Alcohol (0°–25°).

v.	Temperature coefficient.
32	0.702
64	0.768
128	0.822
256	0.956
512	0.930
1024	0.922

Table LXVI.—Temperature Coefficients of Conductivity of Lithium Nitrate in Ethyl Alcohol (0°–25°).

v.	Temperature coefficient.
32	0.308
64	0.370
128	0.408
256	0.458
512	0.476
1024	0.489

Table LXVII.—Temperature Coefficients of Conductivity of Lithium Nitrate in Methyl Alcohol (25, 50, and 75 Per Cent) and Water (0°–25°).

v.	25 per cent.	50 per cent.	75 per cent.
32	1.25	0.97	0.82
64	1.30	1.01	0.86
128	1.35	1.06	0.92
256	1.37	1.11	0.99
512	1.42	1.13	1.04
1024	1.46	1.13	1.07

Table LXVIII.—Temperature Coefficients of Conductivity of Lithium Nitrate in Ethyl Alcohol (50 Per Cent) and Water (0°–25°).

v.	Temperature coefficient.
32	0.83
64	0.88
128	0.91
256	0.97
512	0.99
1024	1.04

Table LXIX.—Comparison of the Molecular Conductivity of Lithium Nitrate in Methyl Alcohol, Water, and Mixtures of these Solvents at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
32	50.00	29.15	23.59	26.67	45.97
64	51.49	29.68	24.49	27.95	50.12
128	52.51	30.15	25.03	28.66	53.95
256	53.40	30.70	25.71	29.51	56.67
512	54.70	31.35	26.35	30.64	60.06
1024	55.30	32.56	27.35	31.91	63.40

Table LXX.—Comparison of the Molecular Conductivity of Lithium Nitrate in Methyl Alcohol, Water, and Mixtures of these Solvents at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
32	91.83	60.56	47.87	47.06	63.51
64	94.62	62.16	49.92	49.52	69.32
128	98.00	63.77	51.50	51.64	74.51
256	99.68	64.96	53.57	54.36	80.57
512	101.3	66.78	54.62	56.68	83.31
1024	102.3	69.02	55.60	58.56	86.46

These values, when plotted (Figs. VII. and VIII.), give curves very similar to those already described in connection with potassium iodide and strontium iodide. The only difference worthy of special mention is the fact that at 0° the molecular conductivity in methyl alcohol rises above that in water.

Ferric Chloride.

It was desired to make a complete investigation of the changes in the conductivity of solutions of ferric chloride in the various solvents. This was desirable on account of the great solubility of the substance in the different alcohols, and because of the large number of ions into which it can dissociate. This part of the investigation, on account of unexpected difficulties met with, and of the time at our disposal, had to be postponed. Some few observations were, however, made, and these are recorded. The ferric chloride used was prepared as follows: Iron filings, which had been washed with alcohol and ether to remove any adhering grease, were heated in a current of pure, dry chlorine in a large combus-

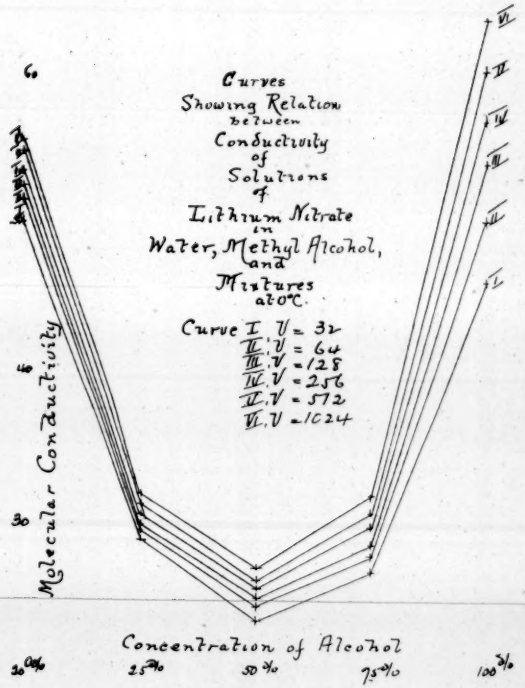

Curves
Showing Relation
between
Conductivity
of
Solutions
of
Lithium Nitrate
in
Water, Methyl Alcohol,
and
Mixtures
at 0°C.
Curve I V = 32
II V = 64
III V = 128
IV V = 256
V V = 512
VI V = 1024
Molecular Conductivity
60
40
30
Concentration of Alcohol
0%
25%
50%
75%
100%

Fig. VII.

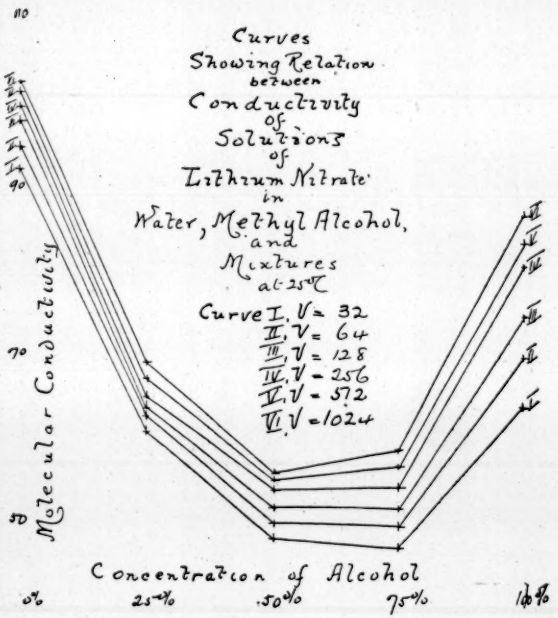


Fig. VIII.

tion tube of hard glass. The ferric chloride formed was allowed to distil into a cooled portion of the tube and then it was redistilled into a wide-mouthed salt bottle. The excess of chlorine was removed by heating the chloride in a current of dry nitrogen. The chloride thus formed dissolved completely in both alcohol and water.

Water solutions were standardized as follows: They were reduced with zinc and sulphuric acid and the ferrous iron de-

termined with standard potassium permanganate. Alcoholic solutions were first precipitated with aqueous ammonia, filtered, washed, dissolved in a little hydrochloric acid, reduced, and titrated as above.

Table LXXI.—Molecular Conductivity af Ferric Chloride in Water.

Ferric chloride, $FeCl_3$. Molecular weight, 162.35.

v.	μ_v 0°.	μ_v 25°.
32	163.7	319.2
64	187.0	370.2
128	213.0	422.6
256	240.0	476.7

These values agree fairly well with those of Goodwin,[1] but are in all cases slightly lower, possibly due to the fact that the conductivity of our solutions was measured immediately after standardization, while Goodwin's had been made up for several months. Accurate measurements at a dilution greater than $v = 256$ could not be made, as hydrolysis took place to a very marked extent, as was noticed by Goodwin in the work just referred to.

Table LXXII.—Temperature Coefficients of Conductivity of Ferric Chloride in Water (0°–25°).

v.	Temperature coefficient.
32	6.22
64	7.32
128	8.38
256	9.47

In mixtures of the alcohols and water the same hydrolysis was found to take place, while in the solutions in absolute alcohol a different change occurred. The solution, originally of a pale straw-color, gradually became lighter and lighter when in contact with the platinum black of the electrodes. This was accompanied by a steady rise in the molecular conductivity, which, at the end of twenty-four hours, was still appreciable. The colorless solution showed only the slightest trace of ferric iron, having apparently been reduced to the ferrous condition. These changes are shown in the following tables :

[1] Phys. Rev., **11**, 193; Ztschr. phys. Chem., **21**, 1.

Table LXXIII.—Table Showing the Changes in the Molecular Conductivity of Ferric Chloride ($v = 512$) with Time, in a Mixture of Methyl Alcohol (50 Per Cent) and Water.

April 8th. P. M.	μ_v 25°.
12.25	....
12.27	130.1
12.29	135.6
12.31	141.8
12.33	145.4
12.36	150.8
12.38	153.9
12.41	156.3
12.45	159.5
12.56	162.4
1.00	166.7
1.10	169.1
1.30	172.9
2.00	175.0
3.00	180.6
4.00	182.2
5.00	183.0

Table LXXIV.—Table Showing the Changes in the Molecular Conductivity of Ferric Chloride ($v = 512$) with Time, in Methyl Alcohol.

April 15th. P. M.	μ_v 25°.
2.15	....
2.18	62.90
2.21	65.47
2.24	67.18
2.28	68.16
2.35	69.64
2.45	71.91
3.00	75.00
3.15	78.06
3.30	81.75
3.46	84.11
4.15	88.59
4.45	92.93
6.15	103.6
April 16th. A. M.	
10.35	132.6
11.15	133.7
P. M.	
2.35	134.3

Summary.

We are led from the preceding study to conclude that the minimum point, discovered by Zelinsky and Krapiwin, is not an isolated phenomenon restricted to the mixtures of methyl alcohol and water, but is much more general. This minimum point in the conductivity has been found for all the salts studied in mixtures of methyl alcohol and water, with the exception of cadmium iodide. Ethyl alcohol and water yield a minimum in the conductivity of all the salts investigated at 0°. At 25° this minimum had disappeared. Mixtures of methyl alcohol and ethyl alcohol do not exhibit this phenomenon, but the conductivity of a salt dissolved in a 50 per cent mixture of methyl and ethyl alcohols is less than the mean of the conductivities of the substance in the pure solvents at the same dilution.

To explain these facts one of us[1] advanced tentatively the following suggestion. According to the theory of Dutoit and Aston it is only those substances whose molecules are polymerized that can dissociate dissolved electrolytes. If this be true, it is probable, since those substances which dissociate dissolved electrolytes also show in general a normal molecular weight for dissolved non-electrolytes, that this breaking down of the polymerized molecule can be accomplished best by another associated molecule. From this it follows that the effect of mixing two associated solvents would be to lower the state of association of one or both until a state of equilibrium is reached. Such a mixture would be that of water and either methyl or ethyl alcohol, or a mixture of methyl alcohol and ethyl alcohol. In these cases, since the molecules are less associated than the constituents, we would expect dissolved electrolytes to show a conductivity lower than that required by the law of mixtures. In every solvent with which we have worked this is exactly what has been observed. In the mixtures of methyl alcohol and water, where the association of the constituents is the greatest, the lowering of conductivity is also the greatest, as would be expected.

In support of the above view that one associated solvent

[1] Lindsay.

can diminish the association of another associated solvent, we have experimental evidence in the results of freezing-point measurements. The molecular weights of the alcohols in water, as determined by the freezing-point method, are normal, while the surface-tension method of Ramsay and Shields shows, beyond question, that the alcohols are associated compounds.

The effect of temperature on the lowering of the conductivity is in accord with the above suggestion. Since the effect of rise in temperature is to lower the state of aggregation of an associated liquid, it would be expected that at the higher temperature the influence of the solvents on each other would be less than at the lower temperature. That such is the case can be seen by comparing the results at 0° with those at 25°.

In conclusion we desire to thank Mr. Kaufman G. Falk for assistance in making the conductivity measurements during the latter part of this investigation.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
May, 1902.

HYDROLYSIS OF TRIACETYLGLUCOSE BY ENZYMES.

BY S. F. ACREE AND J. E. HINKINS.

In a previous article[1] we showed that some bacteria, especially *Bacillus acidi lactici* and *B. sarcina lutea*, when in culture media containing glucose, lactose, etc., generate organic acids, and, furthermore, have the property of causing these organic acids to combine with the sugar to form esters. It was found that, although the bacteria continued to produce acids, the free acid did not increase in quantity, but by titrating the free acid in the cold and then boiling this neutral solution for a short time, more free acid was generated. Hence we guickly guessed that the bacteria, or possibly enzyme-like bodies excreted from them, were causing a part of the free acid to combine with the glucose to form glucose

[1] Read before the International Dental Congress, Paris, Aug. 8, 1900. Dental Cosmos, June, 1901.

esters which, in the cold, were not rapidly saponified by sodium hydroxide, but which, by boiling, were hydrolyzed by the hot water. Hence the amount of the acid combined as ester was determined by titration with N/10 sodium hydroxide after the hydrolysis. Such hydrolysis of ordinary esters or even more complex ones[1] is so well known that it needs no further comment.

Under the conditions of our experiments it was impossible to tell whether the bacteria hydrolyze the glucose esters, as well as cause their formation from glucose and free acids. We afterwards took up this work again with the view of ascertaining if such a reversible process can be realized. Since triacetylglucose can be easily made, and since enzymes, such as pancreatin, emulsion, diastase, etc., can be easily obtained in the market, we began the work by the study of the action of the enzymes on triacetylglucose. We have found that enzymes hydrolyze triacetylglucose into acetic acid and glucose. Furthermore, what few experiments we have carried out in this direction show that the enzymes can also make acetic acid unite with glucose to form esters,—in other words, we have here a reversible process that can be represented as follows when we consider only the formation and hydrolysis of monoacetylglucose, which is, of course, the simplest ester that can be formed by the action of acetic acid on glucose.

$$C_6H_{11}O_5OH + HOOC.CH_3 \rightleftarrows C_6H_{11}O_5CO_2CH_3 + H_2O.$$

One very important reason for starting first with the action of enzymes (not bacteria) on triacetylglucose is that the enzymes do not act upon the products of hydrolysis, namely, glucose and acetic acid, and hence the determination of the amount of hydrolysis is very simple.

When a sterilized solution containing 20 grams of glucose and 5 cc. of glacial acetic acid in 1 liter, and which was the N/11.51 acid, was closed and allowed to stand at a constant temperature of 37° C. for thirty days there was no fermentation, nor was there any change in the strength of the acid, as it was shown by titration at the end of this time to have ex-

[1] Acree: This JOURNAL, **27**, 132; Ber. d. chem. Ges., **38**, 553.

actly the same strength, N/11.51. This same was also true for a part of this solution diluted about three and a half times, so that it was N/37.35 acid. Furthermore, when a 3.2 per cent solution of triacetylglucose, which titrated N/42.44 acid, was left at 0° C. for thirteen days, and kept sterile by means of toluene and thymol, there was no hydrolysis by the water, for titration showed at the end that it was N/42.50. A faintly acid solution of pancreatin was allowed to stand for ten days, but no change in acidity took place. Hence we are very sure that if any changes take place according to the above equation, the enzyme must take part in the reaction or act as a catalytic agent. Hufner,[1] Loew,[2] Nasse,[3] and others, have given us theories to account for the action of ferments, but none are well worked out experimentally. Nasse's hypothesis might be restated as follows: Glucose gives no hydroxyl ions, and hence dilute acetic acid does not act upon it. Suppose that pancreatin has the power to unite with glucose, and that in this double compound the hydroxyl groups of the glucose become hydroxyl ions; then the ionized acetic acid can act upon this double compound, forming water and the double compound, enzyme-acetylglucose, which may break up into the enzyme and acetylglucose. The enzyme which is thus regenerated may then act upon another molecule of glucose (or the acetylglucose), causing other hydroxyl groups to be changed to hydroxyl ions, and hence the process is repeated. If we assume all the above reactions to be reversible, then the hydrolysis of acetylglucose, for instance would be incomplete. But if some steps in the reaction are non-reversible or practically so, then we might have the reaction going completely in one direction. The entire reaction can be represented as follows:

$$C_6H_{11}O_5OH + HAc^1 + \text{enz.} \rightleftharpoons$$
$$\text{enz.}\ C_6H_{11}O_5OH + H + Ac \rightleftharpoons$$
$$\text{enz.}\ C_6H_{11}O_5 + OH + H + Ac \rightleftharpoons$$
$$\text{enz.}\ C_6H_{11}O_5Ac + H_2O \rightleftharpoons$$
$$C_6H_{11}O_5Ac + \text{enz.} + H_2O.$$

[1] Hufner: J. prakt. Chem., N. F., 10, 385 (1874).
[2] Loew: *Ibid.*, 11, 372 (1875); Pflüg. Archiv., 27.
[3] Nasse: Maly's Jb., 1894, 718.
[4] Ac = CH_3CO_2-; enz. = enzyme.

Nasse's hypothesis, however, as applied in the above form, does not easily give us an explanation of the oxidation and reduction reactions accomplished by bacteria and enzymes.

If we look through the literature on enzymes, we find isolated cases where enzymes cause the hydrolysis of substances similar to the above. Probably the best piece of work done was published by Kastle and Loevenhart.[1] They showed that lipase hydrolyzes ethyl butyrate into alcohol and butyric acid, and, further, that lipase is capable of effecting the synthesis of ethyl butyrate from butyric acid and ethyl alcohol; that is, the action of lipase is reversible. Baas[2] found that methyl, phenyl, and ethyl salicylates are hydrolyzed in the intestine of a dog. Schmiedeberg[3] showed that histozyme can hydrolyze hippuric acid into benzoic acid and glycocoll, and Niencki[4] showed that pancreas effects the same hydrolysis.

The triacetylglucose used in this work was made as follows:[5] Forty grams of crystallized glucose and 100 grams of acetic anhydride were mixed in a flask and heated to 100° C. Most of the glucose went into solution immediately, but an oil was left at the bottom. This was soon acted upon by the acetic anhydride, and so violently that the flask had to be cooled to avoid boiling over. Upon warming on the water-bath for three hours, the liquid had assumed a brownish color. This was poured into water in an evaporating dish, and was evaporated to a syrup, then diluted and again evaporated to a syrup. This syrup was shaken out with benzene in a separatory-funnel to extract a small amount of the triacetylglucose for analysis, and the residue was dissolved in 2 liters of water, and used in all the succeeding work. The benzene solution was evaporated to dryness and let stand in a desiccator over lime. The triacetylglucose remained behind as a thick oil with a faint smell of acetic acid. This oil was analyzed, and the analysis proved it to be triacetylglucose.

[1] This JOURNAL, **24**, 491.
[2] Ztschr. physiol. Chem., **14**, 416 (1890).
[3] Arch. f. exper. Path. u. Pharm., **14**, 379 (1881).
[4] *Ibid.*, **20**, 367 (1886).
[5] Schützenberger and Naudin: Bull. Soc. Chim., **13**, 204.

0.5186 gram substance gave 0.8945 gram CO_2 and 0.2743 gram H_2O.

	Calculated for $C_{12}H_{18}O_9$.	Found.
C	47.06	47.04
H	5.88	5.94

As this analysis would not show the composition of the main portion of the triacetylglucose, but only of that portion extracted with benzene, the 2 liters of triacetylglucose solution were analyzed as follows:

If the triacetylglucose (?) solution were treated with an alkali and boiled, the acetyl groups would be split off by hydrolysis and would neutralize part of the alkali; it should titrate as if it were N/3.30 acid. We titrated the boiling triacetylglucose solution against N/5 potassium hydroxide; when nearly neutralized the solution became slightly brown, so that the end of the titration could not be sharply detected. The results showed that the triacetylglucose solution was apparently N/3.44 acid; in other words, there seemed to be about 2.9 acetyl groups, instead of 3, to each glucose molecule. As this makes really no difference, as far as our problem is concerned, we shall use the expression "triacetylglucose solution," when speaking of the above solution.

	N/5 KOH solution. cc.	Triacetylglucose solution. cc.
1	13.00	8.86
2	17.24	11.71
3	20.64	14.39
4	28.04	19.42

Strength of triacetylglucose solution, N/3.44.

The main portion of the triacetylglucose, which was dissolved in the 2 liters of water, had a small amount of acetic acid in it. This amount was determined by titration with N/5 potassium hydroxide, using phenolphthalein as the indicator, this being the indicator used in all titrations.

	N/5 KOH solution. cc.	Triacetylglucose solution. cc.
1	0.67	5.56
2	0.90	7.08
3	1.00	8.47

Therefore, 1 cc. of the triacetylglucose solution equals 0.1218 cc. of the N/5 potassium hydroxide solution, or is N/41 in acid strength. This triacetylglucose solution was kept in an ice-box during all the work, and titrations of the acid strength were made from time to time. These titrations showed but little variation among themselves; in other words, triacetylglucose is not hydrolyzed to any appreciable extent by water at 0° C.

But a rise in temperature produces a very important change. As is well known, previous experiments by different men have all shown that in esterification or saponification reactions the rise in temperature increases the velocity of the change, but the amount of change is independent of the temperature. A solution of triacetylglucose that remained about N/42.50 for thirteen days, when kept at 0° C., was then kept at 37° C. An increase in the amount of hydrolysis was immediately noticeable, and the acidity in two days was N/35.7. We seem to have in triacetylglucose an exception to the above law. Whether the triacetylglucose is not hydrolyzed by water at 0° C., and is at 37° C., or whether the hydrolysis is so very slow at 0° C., that the acidity is practically unchanged in thirteen days, we cannot say at present.

The action of the enzymes, pancreatin, amylopsin, emulsin, maltase, diastase, takadiastase, etc., was tried. One hundred cc. of the triacetylglucose were treated with 0.5 gram to 1 gram of the enzyme to be studied, and were kept at a constant temperature of 0° C. Titrations were made at the beginning, and also every day or two, to determine the increase in the amount of acid present, and unless stated otherwise, the titrations of a given solution were made at the same time on each day; that is, exactly twenty-four hours, or a multiple of this time, apart. In some cases the enzyme itself has a slightly acid reaction, and the proper corrections have been made in the succeeding tables for this. In all cases studied, the enzyme hydrolyzed triacetylglucose into glucose and acetic acid. The amount of glucose present did not vary, that is, the enzyme did not use up any glucose. Some enzymes hydrolyzed only a small amount of the triacetylglucose, while

others effected relatively a large amount of hydrolysis. Pancreatin seemed to be the most active. Not only does pancreatin hydrolyze triacetylglucose, but it is also capable of effecting the union of acetic acid with glucose to form the glucose ester. Only a few experiments were carried out in this line, but these were carefully made and, together with the work of the previous paper, seem to prove that we are dealing here with a reversible action.

As most of the experiments were carried out at 0° C., we thought that it would be interesting to carry out some at 37° C. We find that the activity of pancreatin is greatly increased by a rise in temperature. As will be seen below, 0.5 gram of pancreatin in 100 cc. of triacetylglucose which, at 37° C., had become about constant at N/33 in acid strength, became N/26 in two days. The increase in acidity was N/123. One gram of pancreatin, or twice the above amount, in 100 cc. of triacetylglucose at 0° C. required two days to produce this increase in acidity; pancreatin then showed twice as much activity at 37° as it did at 0°.

Many experiments show that in the hydrolysis of cane sugar, ethyl acetate, etc., by a given acid, the amount of hydrolysis is proportional to the amount of acid used. Experiments in which we used varying amounts of pancreatin in 100 cc. of triacetylglucose solution, showed that the amount of hydrolysis is dependent upon, and very nearly proportional to, the amount of enzyme present. The hydrolysis of the triacetylglucose is in no case complete. This does not necessarily show that the reaction is reversible, as the acetic acid produced would inhibit, to a certain extent, the action of the enzyme, and would finally cause the reaction to come to a standstill.

Experiment to Determine whether Glucose and Acetic Acid React at 0° or at 37°.—Twenty grams of recrystallized glucose melting at 147° and 5 cc. of glacial acetic acid were dissolved in 1 liter of water and titrated against N/5 potassium hydroxide solution, using phenolphthalein as indicator. The acid strength was N/11.70. After sterilizing at 120° for five minutes, the acid strength was N/11.51. The solution was kept

sterile in a flask with a siphon, so that portions of the liquid could be withdrawn without infecting the solution. Two days later the solution showed the same acid strength, N/11.51. Nine days later the acid strength had not changed, and the sterilized solution was then kept at a constant temperature of 37°. On the tenth day the acid strength was N/11.47, and on the fourteenth day was N/11.51. This shows that in a dilute solution of glucose and acetic acid there is no appreciable action and we need not consider this in our further work.

Experiment to Determine whether Pancreatin Acts upon Glucose in a Sterilized Solution.—A solution of 5 grams of pure glucose (melting at 147°) in 100 cc. of water was sterilized and cooled to 0° C. To this was added 0.5 gram of pancreatin that had been washed several times with absolute alcohol. To this solution was added a small amount of a mixture of thymol and toluene to keep the solution sterile. The mixture was thoroughly shaken and allowed to remain in the ice-chest a short time. Ten cc. were withdrawn by means of a sterilized pipette and titrated against N/5 potassium hydroxide, using phenolphthalein as indicator. One drop of the potassium hydroxide solution, or 0.03 cc., was enough to produce a decided pink color. The solution was allowed to remain in the ice-box four days, but no change was visible. No gas was given off, showing that no fermentation had taken place. At the end of the fourth day 10 cc. of the solution were removed, as before, and titrated. One drop, or 0.03 cc., of the potassium hydroxide solution was again sufficient to produce a decided pink color. Enzymes do not ferment sugars, and in our further experiments upon the action of enzymes on triacetylglucose we are sure that there is no formation of acid from part of the glucose formed by the hydrolysis of the triacetylglucose.

Experiment to Determine whether Pancreatin in Sterilized Water Decomposes and Forms an Acid or Alkaline Solution.—One-half gram of pancreatin was added to 100 cc. of distilled water and 1 cc. of toluene was added. The solution was kept

at 0° C. It was slightly acid, as the following titrations show :

Titration at the Beginning.

N/5 potassium hydroxide solution.	Pancreatin solution.	Acidity.
cc.	cc.	
0.12	5.00	
0.17	7.00	N/207

Titration after Forty-eight Hours.

0.11	5.00	
0.24	10.00	N/215

The acid strength of the pancreatin solution is N/215, a hardly perceptible change from the above. In further experiments, then, we can disregard the decomposition of the enzyme itself.

Triacetylglucose Solution.—As stated above, this stock solution was kept sterile by means of toluene and thymol, and was kept in an ice-box. Titrations were made from time to time to see if any hydrolysis could be detected. As seen from the tables there was no appreciable change in the acid strength, and no fermentation was ever noticed.

Titration at the Beginning.

N/4 potassium hydroxide solution.	Triacetylglucose solution.	Acidity.
cc.	cc.	
0.60	5.09	
0.75	6.37	
0.95	7.95	N/42.45

Titration after Twenty-four Hours.

0.59	5.03	
0.89	7.34	
1.04	8.60	N/41.85

Titration after Forty-eight Hours.

0.60	5.09	
0.88	7.14	
1.11	8.83	N/40.65

Titration after One Hundred and Twenty Hours.

0.58	5.00	
0.86	7.00	N/42

Titration after One Hundred and Forty-four Hours.

N/5 potassium hydroxide solution. cc.	Triacetylglucose solution. cc.	Acidity.
0.57	5.00	
0.85	7.00	N/42.50

Other titrations were made after this time but no appreciable change was noticed.

Experiment to Determine the Change in a Solution of Triacetylglucose by Raising the Temperature from 0° to 37°.—As we expected to carry out experiments in which the solution of triacetylglucose would be subjected to a change in temperature from 0° to 37°, it was thought necessary to determine whether this solution itself would change in acid strength upon heating. A sterilized solution of triacetylglucose was titrated and then put into an oven having a constant temperature of 37°. As will be seen from the tables, the amount of hydrolysis was increased by a rise in temperature.

Titration at the Beginning.

N/5 potassium hydroxide solution. cc.	Triacetylglucose solution. cc.	Acidity.
0.60	5.00	
0.86	7.00	N/41
Titration after Twenty-four Hours.		
0.66	5.00	
0.95	7.00	N/37.5
Titration after Forty-eight Hours.		
0.70	5.00	
1.41	10.00	N/35.7

In two days the acidity of the triacetylglucose solution increased from N/41 to N/35.7. As will be seen below, this solution finally became constant at about N/33.

Hydrolysis of Triacetylglucose by Pancreatin.—A solution of 1 gram of pancreatin in 100 cc. of the above solution of triacetylglucose was made, and the acid strength was determined by titration to be N/40.65. This, as were all of the other solutions, was kept sterile by means of toluene and thymol and was kept at constant temperature of 0°.

Titration after Forty-eight Hours.

N/5 potassium hydroxide solution. cc.	Pancreatin solution. cc.	Acidity.
1.15	7.19	
1.42	8.71	
1.85	11.10	N/30.64

Titration after Ninety-six Hours.

1.00	5.00	
1.49	7.00	N/24.25

Titration after Two Hundred and Forty Hours.

1.18	5.00	
1.62	7.00	N/21

Hydrolysis of Triacetylglucose by Amylopsin.—One gram of amylopsin was dissolved in 100 cc. of triacetylglucose solution and kept sterile by means of toluene. The acidity at first was N/41.

Titration after Twenty-four Hours.

N/5 potassium hydroxide solution. cc.	Amylopsin solution. cc.	Acidity.
0.70	4.95	
1.02	7.15	
1.28	8.95	N/35.10

Titration after Ninety-six Hours.

0.80	5.00	
1.20	7.00	N/30.20

Titration after Two Hundred and Forty Hours.

1.00	5.00	
1.40	7.00	N/25

Hydrolysis of Triacetylglucose by Emulsin.—This solution was made by adding 1 gram of emulsin to 100 cc. of the solution of triacetylglucose, and was kept sterile by means of thymol and toluene. It titrated N/50 acid at first.

Titration after Twenty-four Hours.

N/5 potassium hydroxide solution.	Emulsin solution.	Acidity.
cc.	cc.	
0.75	6.01	
1.05	8.25	
1.20	9.72	N/39.93

Titration after Ninety-six Hours.

0.60	5.00	
0.88	7.00	N/40.40

Titration after Two Hundred and Sixty-four Hours.

0.62	5.00	
0.87	7.00	N/40.50

We see that emulsin hardly hydrolyzes triacetylglucose even in ten days.

Hydrolysis of Triacetylglucose by Maltase.—Fresh malt was powdered and sifted and 4 grams added to 100 cc. of the solution of triacetylglucose. This was kept sterile in an ice-box. The solution was N/42.44 at first.

Titration after Forty-eight Hours.

N/5 potassium hydroxide solution.	Maltase solution.	Acidity.
cc.	cc.	
0.69	4.62	
0.97	6.64	
1.20	8.24	N/34

Titration after Seventy-two Hours.

0.79	5.24	
1.10	7.33	
1.49	10.02	N/33.35

Titration after Ninety-six Hours.

0.93	5.37	
1.11	6.52	
1.35	8.00	N/29.30

Titration after One Hundred and Sixty-eight Hours.

0.95	5.00	
1.39	7.00	N/25.75

Titration after Three Hundred and Thirty-six Hours.

1.13	5.00	
1.57	7.00	N/22.20

Hydrolysis of Triacetylglucose by Diastase.—This solution was made by adding 2 grams of diastase to 100 cc. of the solution of triacetylglucose, and was kept sterile by means of thymol. The temperature was kept at 0° C. The acidity at first was N/40.90, as shown by the tables.

Titration of Fresh Solution.

N/5 potassium hydroxide solution. cc.	Diastase solution. cc.	Acidity.
0.63	5.10	
0.91	7.55	
1.19	9.70	N/40.90

Titration after Twenty-four Hours.

0.96	7.60	
1.55	12.15	
2.05	16.15	N/39.39

Titration after Forty-eight Hours.

0.70	5.38	
0.90	6.93	
1.11	8.45	N/38.62

Titration after One Hundred and Twenty Hours.

0.66	5.00	
0.98	7.00	N/37.8

Titration after Two Hundred and Eighty-eight Hours.

0.71	5.00	
1.01	7.00	N/35

Hydrolysis of Triacetylglucose by Takadiastase.—This solution was made by adding 0.5 gram of takadiastase to 100 cc. of the solution of triacetylglucose. It was kept in an ice-box. The acid strength was N/41.

Titration after Twenty-four Hours.

N/5 potassium hydroxide solution. cc.	Takadiastase solution. cc.	Acidity.
0.76	5.00	
1.10	7.00	N/32.35

Titration after Ninety-six Hours.

0.87	5.00	
1.19	7.00	N/29

Titration after One Hundred and Sixty-eight Hours.

N/5 potassium hydroxide solution.	Takadiastase solution.	Acidity.
cc.	cc.	
0.93	5.00	
1.32	7.00	N/27

Effect of Rise in Temperature on the Amount of Hydrolysis by Pancreatin.—One-half gram of pancreatin was added to 100 cc. of a solution of triacetylglucose that had been kept at 37° for some time, and that had become constant at about N/33. This solution was kept sterile by means of toluene and was kept at a constant temperature of 37°.

Titration at First.

N/5 potassium hydroxide solution.	Pancreatin solution.	Acidity.
cc.	cc.	
0.74	5.00	
1.08	7.00	N/33

Titration after Twenty-four Hours.

0.89	5.00	
1.22	7.00	N/28

Titration after Forty-eight Hours.

0.98	5.00	
1.89	10.00	N/26

As the table shows, the increase in acidity in forty-eight hours was N/123, which is approximately the increase produced by 1 gram of pancreatin, or twice the amount here used, in the same volume of the cold solution in the same time. The activity of pancreatin, then, is approximately twice as great at 37° as it is at 0°.

Experiments to Determine the Relation between the Amount of Pancreatin Used and the Amount of Hydrolysis.—Three solutions were made containing 0.25 gram, 0.5 gram, and 0.75 gram, respectively, of pancreatin in 100 cc. of the solution of triacetylglucose. These were kept at 0° and were sterilized by means of toluene. As the tables show, the amount of hydrolysis is approximately proportional to the amount of enzyme used. The tables show the amount of acetic acid

formed in one liter. The solutions were all approximately N/41 at first.

Titration after Forty-eight Hours.

With solution containing 0.25 gram pancreatin.

N/5 potassium hydroxide solution.	Pancreatin solution.	Acidity.	Acetic acid formed in 1 liter.
cc.	cc.		Gram.
0.69	5.00		
0.96	7.00	N/36	0.20

With solution containing 0.5 gram pancreatin.

0.77	5.00		
1.11	7.00	N/32	0.41

With solution containing 0.75 gram pancreatin.

0.83	5.00		
1.18	7.00	N/29.5	0.57

As can be seen, the figures 0.20, 0.41, and 0.57 gram are very nearly in the ratios 1 : 2 : 3.

Titration after Ninety-six Hours.

With solution containing 0.25 gram pancreatin.

N/5 potassium hydroxide solution.	Pancreatin solution.	Acidity.	Acetic acid formed in 1 liter.
cc.	cc.		Gram.
0.68	5.00		
0.97	7.00	N/36.5	0.18

With solution containing 0.5 gram pancreatin.

0.79	...		
1.10	7.00	N/32	0.42

With solution containing 0.75 gram pancreatin.

0.87	5.00		
1.19	7.00	N/28	0.58

Here again, the ratios of the amounts of acid generated are approximately the same as the ratios of the amounts of pancreatin used.

Titration after One Hundred and Forty-four Hours.

With solution containing 0.25 gram pancreatin.

N/5 potassium hydroxide solution.	Pancreatin solution.	Acidity.	Acetic acid formed in 1 liter.
cc.	cc.		Gram.
0.72	5.00		
0.99	7.00	N/35	0.25

With solution containing 0.5 gram pancreatin.

0.83	5.00		
1.18	7.00	N/30	0.54

With solution containing 0.75 gram pancreatin.

0.91	5.00		
1.25	7.00	N/27.5	0.72

As will be seen from the above tables, the amount of triacetylglucose hydrolyzed is very nearly proportional to the amount of pancreatin present.

Experiment to Determine whether Pancreatin Can Cause Esterification in a Mixture of Glucose and Acetic Acid.—Twenty grams of glucose (melting-point 147°) and 5 cc. of glacial acetic acid were dissolved in 1 liter of water. Fifty cc. of this solution were diluted to 200 cc., and to this solution were added 0.5 gram of pancreatin and 2 cc. of toluene. The solution was kept at 0°.

Titration at First.

N/5 potassium hydroxide solution.	Pancreatin solution.	Acidity.
cc.	cc.	
0.68	5.00	N/37.35

Titration after Twenty-four Hours.

0.66	5.00	
0.93	7.00	N/37.75

Titration after Seventy-two Hours.

0.63	5.00	
0.89	7.00	
1.52	12.00	N/39

Titration after Ninety-six Hours.

0.62	5.00	
0.88	7.90	
1.51	12.00	N/40

Titration after One Hundred and Twenty Hours.

N/5 potassium hydroxide solution.	Pancreatin solution.	Acidity.
cc.	cc.	
0.63	5.00	
1.25	10.00	N/40

As the tables show, the acidity decreased from N/37.35 to N/40. When the acidity had decreased to N/40 we noticed that the pink color of the solution that had been titrated would nearly disappear after a short time, indicating the presence of glucose acetates, which were slowly saponified by the potassium hydroxide. As the decrease in acidity in this experiment is only a very small amount, we do not think this decisive. We are therefore carrying out other experiments to determine this point more carefully. But when these results are taken in connection with the previous paper, in which it was clearly shown that such esters were formed by bacteria, it is very probable that further experiments will show decisively that enzymes can form glucose acetates from, as well as hydrolyze them into, glucose and acetic acid. The work has been unavoidably interfered with, but we shall now take it up again, and the above is intended as a preliminary announcement.

CHICAGO, July 15, 1902.

Contribution from the Chemical Laboratory of the University of Texas.

RING CONDENSATIONS OF THE ESTERS OF URAMIDO AND SEMICARBAZINO ACIDS WITH SODIUM ALCOHOLATE.

BY J. R. BAILEY.

INTRODUCTION.

In an investigation of the ethyl ester of hydantoic acid[1] the author, in connection with C. P. Norby, discovered that this substance, when treated with sodium or potassium alcoholate, readily passes into the sodium or potassium salt, respectively, of hydantoin. Further investigation has shown that sodium

[1] The work on this substance was finished when Harries reported its discovery and its conversion into hydantoin by means of hydrochloric acid (Ber. d. chem. Ges., 33, 3418). The publication of this work has been deferred until now, owing to the withdrawal of Mr. Norby from the University and a year's absence of the author.

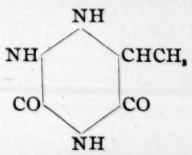
alcoholate can be employed as a general reagent to effect ring condensations with the esters of both uramido and semicarbazino acids. This use of sodium alcoholate may be regarded as an extension of Michael's method for the preparation of cyclical ureides.[1] The experiments herein described weer carried out for the most part in each case with not more than 1 or 2 grams of substance and were seldom repeated. The yields when given are, therefore, not to be regarded as the maximum yields to be obtained in working with large quantities of material. Our efforts were rather directed toward establishing the general applicability of the reaction. As the reaction takes place in the cold, and as in none of the condensations a by-product is obtained, this reaction, where applicable, may be considered as giving an almost quantitative yield.

All attempts to split off alcohol from the ethyl ester of the semicarbazone of pyruvic acid,

$$NH_2CONHN = C(CH_3)COOC_2H_5,$$

were futile. This is rather peculiar, in view of the fact that the ethyl ester of semicarbazinopropionic acid readily passes into the corresponding dihydromethyldioxy-α-triazine. This latter condensation takes place especially readily with sodium alcoholate thus:

$NH_2CONHNHCH(CH_3)COOC_2H_5 \rightarrow$



(In form of sodium salt.)

The ethyl ester of semicarbazinopyruvic acid[2] can be obtained by oxidizing the ethyl ester of semicarbazinopropionic acid, and differs from it in having two hydrogen atoms less. Furthermore, the methyldioxy-α-triazine sought is easily obtained by oxidizing the dihydrotriazine referred to above.[3]

[1] J. prakt. Chem., [2] **35**, 456.
[2] Ann. Chem. (Liebig), **303**, 87.
[3] *Ibid.*, p. 82.

Thiele and Dralle report similar failures to effect triazine condensations in the hydrazone series.[1] It would be interesting to know the action of sodium alcoholate on the oxidation-product of the ethyl ester of semicarbazino-iso-butyric acid but, because of lack of material, this part of the investigation has been deferred. Here the oxidation-product would not be a semicarbazone but an azo compound,

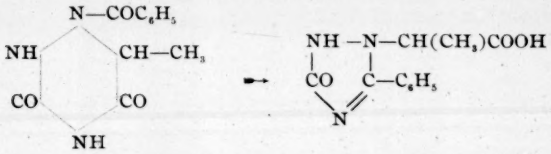
$$NH_2CON = NC(CH_3)_2COOC_2H_5,$$

with two hydrogen atoms less than the corresponding hydrazo compound.

The behavior of the benzoyl derivative of the ethyl ester of semicarbazinopropionic acid,

$$NH_2CONHN(COC_6H_5)CH(CH_3)COOC_2H_5,$$

towards sodium alcoholate was investigated to see whether a triazol condensation with the elimination of water, or a triazine condensation with the elimination of alcohol would be effected. The reaction goes normally with the formation of a benzoyltriazine. The benzoyl derivative thus obtained can, however, by the action of an aqueous alkali, be converted into 3-oxy-5-phenyltriazol-1-propionic acid :



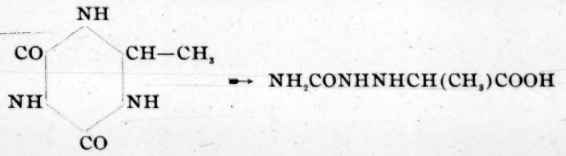
This reaction, which might at first seem rather peculiar, can be very easily interpreted as follows : The alkali splits the triazine ring forming the alkali salt of benzoylsemicarbazinopropionic acid, and, as Bailey and Acree showed, this latter substance, under the influence of an alkali, passes with the elimination of water into 3-oxy-5-phenyltriazol-1-propionic acid.[2]

The behavior of the ethyl ester of semicarbazinopropionic

[1] Ann. Chem. (Liebig), **302**, 275.

[2] Ber. d. chem. Ges., **33**, 1525.

acid toward alcoholic potash is of considerable theoretical interest. When to this ester, in absolute alcohol, alcoholic potash is added, there begins, after a few minutes, a separation of dihydromethyldioxy-α-triazine. The normal action of alcoholic potash on an ester is saponification, but its action here is to effect a ring condensation by splitting off alcohol. This reaction is all the more peculiar in that there is no salt formed by the triazine and the potash, and because, furthermore, the triazine here formed, which is a cyclical amide, is very unstable toward aqueous alkalies, being hydrolyzed on treatment with 0.5 molecule of barium hydroxide to semicarbazinopropionic acid, thus:



It was of interest to determine whether the ethyl ester of hydantoic acid would undergo a similar condensation with alcoholic potash to hydantoin, and it was found that the normal reaction of saponification takes place.

A very satisfactory modification of Fischer's method of esterification was used in the case of hydantoic acid and the two semicarbazino acids worked with. These substances are very sensitive toward mineral acids, and in the case of hydantoic acid, where even as dilute a solution of hydrochloric acid in alcohol as 3 per cent was used, it was found that if the solution were boiled all of the substance to be esterified was converted into hydantoin. However, if hydantoic acid or the semicarbazino acids are allowed to stand with 3 per cent alcoholic hydrochloric acid two weeks, esterification, without ring condensation, is effected. This method of esterification is especially welcome in the series of semicarbazino fatty acids, where in some cases all attempts to prepare the esters from the nitrils, with the imido

ethers as intermediary products, have been unsuccessful; for example, the methylimido ether of semicarbazinopropionic acid was not obtained by the action of alcoholic hydrochloric acid or alcoholic sulphuric acid on the nitril, although these methods give the corresponding ethyl and propylimido ethers. Repeated attempts to prepare esters of semicarbazinoisobutyric acid by the action of alcoholic solutions of acids on the nitril of semicarbazinoisobutyric acid gave in no case even a trace of the ester.

EXPERIMENTAL PART.

I.

Condensation of the Esters of Uramido Acids to Hydantoins.[1]

The Ethyl Ester of Hydantoic Acid.—This substance is best prepared according to the method of Harries referred to above, but it may also be prepared by the esterification of hydantoic acid: Ten grams of hydantoic acid were put into 240 cc. of alcoholic hydrochloric acid, whereupon, after a few minutes' shaking, complete solution was effected. After standing two weeks in the cold, the solution was neutralized with sodium bicarbonate and the alcohol removed by evaporation. The residue, when extracted with alcohol, yielded 12.37 grams of ester, or 97 per cent of the theoretical. In an experiment in which hydantoic acid in 3 per cent alcoholic hydrochloric acid was boiled for several hours, all of the acid was converted into hydantoin. The latter substance was identified by its solubility and melting-point, and by a nitrogen determination.

0.0923 gram substance gave 22.9 cc. N at 18° and 750 mm.

	Calculated for $C_5H_4O_2N_2$.	Found.
N	28.00	28.27

The ethyl ester of hydantoic acid gives, with sodium or potassium alcoholate, the corresponding salt of hydantoin. However, unlike the ethyl ester of semicarbazinopropionic acid, it reacts normally with alcoholic potash, giving the

[1] The investigation of the hydantoic acid derivatives and hydantoin was carried out conjointly with C. P. Norby.

potassium salt of hydantoic acid.[1] This salt decomposes at about 130°.

0.1878 gram substance gave 0.1040 gram K_2SO_4.

	Calculated for $C_3H_4O_3N_2K$.	Found.
K	25.00	24.82

The amide of hydantoic acid can be prepared by allowing the ester to stand with alcoholic ammonia. It melts with evolution of gas at 204°.

0.1340 gram substance gave 0.1515 gram CO_2 and 0.0735 gram H_2O.

0.1391 gram substance gave 42.4 cc. N at 12° and 756 mm.

	Calculated for $C_3H_7O_2N_3$.	Found.
C	30.77	30.83
H	5.98	6.09
N	35.90	35.99

The nitril of hydantoic acid[2] can be obtained by bringing together in concentrated aqueous solutions potassium cyanate and the nitril of glycocoll hydrochloride in molecular proportions.[3] It crystallizes from water in prisms, which melt at 139° to a clear liquid, and, on boiling in aqueous solution with 0.5 molecule of barium hydroxide, is saponified to hydantoic acid.

0.1628 gram substance gave 59.5 cc. N at 13° and 752.5 mm.

	Calculated for $C_3H_3ON_3$.	Found.
N	42.42	42.76

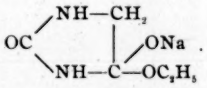
Salts of Hydantoin.—When concentrated solutions of sodium alcoholate and the ethyl ester of hydantoic acid in molecular proportion are mixed, the sodium salt of hydantoin immediately separates as a fine, pulverulent precipitate. After being washed with alcohol and ether, and dried at 110° for several hours, the salt is sufficiently pure for analysis. The substance is only sparingly soluble in alcohol and, although

[1] Ann. Chem. (Liebig), **136**, 281.

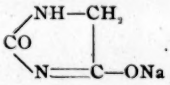
[2] This work was completed when Klages announced the method of preparation of this substance. However, he gives no analytical data or properties of the substance in proof of its constitution (J. prakt. Chem., [2], **63**, 188).

[3] Ber. d. chem. Ges., **27**, 59.

readily soluble in water, probably with hydrolysis, does not deliquesce in the air. Two grams of ester gave 2.06 grams of the air-dried sodium salt of hydantoin; the theoretical yield for $NaC_5H_7O_4N_2$ is 1.67 grams. This yield indicates that the initial reaction-product may possibly be constituted as follows:



And that this, on heating, or more slowly *in vacuo*, splits off alcohol, giving



The first analyses of the sodium salt made were carried out with a sample that was allowed to stand *in vacuo* several days over sulphuric acid and it gave results too low for the simple sodium salt of hydantoin and too high for this salt plus 1 molecule of alcohol. Analysis of sample dried *in vacuo*.

0.1858 gram substance gave 32.1 cc. N at 12°.5 and 754 mm.

0.2201 gram substance gave 0.1108 gram Na_2SO_4.

	Calculated for $C_5H_7O_4N_2Na + C_2H_6O$.	Found.
N	16.67	20.30
Na	13.69	16.31

Analysis of sample dried at 110° for four hours:

0.1211 gram substance gave 23.9 cc. N at 12° and 748 mm.

0.2371 gram substance gave 0.1380 gram Na_2SO_4.

	Calculated for $C_5H_5O_4N_2Na$.	Found.
N	22.95	23.05
Na	18.85	18.88

The constitution of the salts of hydantoin will be further investigated and the results announced later.

The potassium salt can be obtained in the same way as the sodium salt by the action of potassium alcoholate on the ethyl

ester of hydantoic acid. For the analysis the sample was dried at 110°.

0.2670 gram substance gave 45.3 cc. N at 12° and 754 mm.
0.1483 gram substance gave 26.1 cc. N at 16° and 746 mm.
0.2666 gram substance gave 0.1681 gram K_2SO_4.

	Calculated for $C_3H_3O_2N_2K$.	Found. I.	II.
N	20.29	19.98	20.13
K	28.26	28.26	....

Hydantoin can be prepared from its sodium or potassium salt by making concentrated aqueous solutions of the latter slightly acid with hydrochloric acid. Hydantoin prepared in this way proved to be identical with a sample prepared according to the method of Harries. Harries' method of preparation is, however, to be preferred, as it allows a direct and almost quantitative conversion of the ethyl ester of hydantoic acid into hydantoin without the formation of any inorganic by-products. In working with small quantities of substance, the yield of hydantoin by the sodium alcoholate method is about 80 per cent of the theoretical. A sample of hydantoin obtained by this method gave the following results on analysis:

0.2832 gram substance gave 0.3735 gram CO_2 and 0.1027 gram H_2O.

0.1174 gram substance gave 28.5 cc. N at 16°.5 and 760 mm.

	Calculated for $C_3H_4O_2N_2$.	Found.
C	36.00	35.97
H	4.00	4.03
N	28.00	28.24

The Ethyl Ester of Lacturaminic Acid, $NH_2CONHCH(CH_3)COOC_2H_5$.—This ester can be prepared similarly to the ester of hydantoic acid, by treatment of the hydrochloride of the ethyl ester of alanine with potassium cyanate. It is readily soluble in water, chloroform, and alcohol; difficultly soluble in ether and petroleum ether. The substance is best purified by crystallization from benzene. It is thus obtained in the form of a matted mass of very slen-

der, short needles, as seen under the microscope, and melts at 100° to a clear liquid.

0.1692 gram substance gave 27.6 cc. N at 24°.5 and 749 mm.

0.1834 gram substance gave 29.8 cc. N at 25° and 746 mm.

0.2946 gram substance gave 0.4838 gram CO_2 and 0.1982 gram H_2O.

	Calculated for $C_6H_{12}O_3N_2$.	Found. I.	II.
C	45.00	44.79	....
H	7.50	7.47	....
N	17.50	17.97	17.78

The ethyl ester of lacturaminic acid, when treated in alcoholic solution with sodium alcoholate, passes into the sodium salt of lactylurea. As both the sodium and potassium salts separate as a gelatinous mass, difficult to filter, they were not isolated. The method employed in the preparation of lactylurea can be used to advantage where it is not desired to isolate the salt of the alcoholate condensation-product. The reaction-product of the alcoholate and the ester is poured into a very little water, kept slightly acid with hydrochloric acid, and, after neutralization of the alcoholate, the excess of hydrochloric acid is neutralized with ammonia. The solution is then evaporated and the residue extracted with any suitable solvent, usually alcohol. By this method a yield of about 85 per cent of lactylurea can be obtained from the ethyl ester of lacturaminic acid. Prepared in this way, the substance has the properties given by Heinz.[1] Crystallized from alcohol, containing 15 per cent of ether, lactylurea melts at 148°, whereas Heinz gives 140° as the melting-point of the substance crystallized from water.

0.1977 gram substance gave 44.6 cc. N at 25° and 750 mm.

	Calculated for $C_4H_6O_2N_2$.	Found.
N	24.56	24.83

The Ethyl Ester of γ-Phenylhydantoic Acid, $C_6H_5NHCONHCH_2COOC_2H_5$.—Two grams of the ethyl ester of glycocoll hydrochloride and 1.28 grams of sodium bicarbonate are dissolved in 25 cc. of ice-water and then 1.78 grams of

[1] Ann. Chem. (Liebig), **169**, 124.

phenyl isocyanate added. In order to thoroughly emulsify the isocyanate, the mixture is shaken vigorously, when, after a few minutes, the ester of phenylhydantoic acid separates out. Two grams of the ester of glycine hydrochloride gave 2.6 grams of the ester of phenylhydantoic acid. The ester can be purified by crystallization from dilute alcohol or benzene. It crystallizes in slender needles that melt to a clear liquid at 108° to 109°.

0.2342 gram substance gave 27.7 cc. N at 27° and 748 mm.

0.2938 gram substance gave 0.6452 gram CO_2 and 0.1669 gram H_2O.

	Calculated for $C_{11}H_{14}O_3N_2$.	Found.
C	59.46	59.89
H	6.31	6.31
N	12.61	12.84

The ethyl ester of γ-phenylhydantoic acid reacts with sodium alcoholate giving γ-phenylhydantoin, a substance described by Guareschi.[1] The sodium salt, if formed here, is soluble in alcohol and the hydantoin must be isolated by the method described under lactylurea. The hydantoin prepared in this way was compared with some made according to the method of Guareschi and the two samples proved to be in every respect identical.

0.2426 gram substance gave 36.2 cc. N at 28° and 746 mm.

	Calculated for $C_9H_8O_2N_2$.	Found.
N	15.91	16.08

γ-Phenylhydantoic acid can be made from γ-phenylhydantoin by boiling the latter for a few minutes with a barium hydroxide solution. On acidifying the solution the acid separates out and can be purified by crystallization from alcohol. It crystallizes in short, slender needles, that melt with evolution of gas at 197°.

0.1393 gram substance gave 18.8 cc. N at 28° and 751 mm.

	Calculated for $C_9H_{10}O_3N_2$.	Found.
N	14.43	14.64

[1] Beilstein, Vol. II., p. 383.

II.

Condensation of the Esters of Semicarbazino Acids to Triazines.

The semicarbazinopropionitril,

$$NH_2CONHNHCH(CH_3)CN,$$

used in this work was prepared according to the method of Thiele and Bailey[1] with the following modifications: Almost absolute prussic acid was used instead of a 60 per cent solution, and to every 500 cc. were added 2 cc. of strong hydrochloric acid. The first modification has the advantage that the nitril can be much more readily isolated than when a dilute prussic acid is employed, and the second modification prevents the prussic acid from polymerizing.

The semicarbazinopropionic acid[2] used in our experiments was prepared by saponifying semicarbazinopropionitril with barium hydroxide.[3] In this method of preparation the nitril is allowed to stand one week, dissolved in twenty-five times its weight of water, with 0.5 molecule of barium hydroxide, in order to effect a conversion of the nitril into the amide, and then the solution is boiled until the smell of ammonia disappears. After the removal of the barium as sulphate the solution is evaporated to a small bulk and the acid allowed to crystallize out. Certain modifications of this process, looking toward a better yield, are now being tried and will be published later.

The following modification of the process of Thiele and Bailey[4] was employed in the preparation of the ethyl ester of semicarbazinopropionic acid: Thirty-eight grams of nitril were put into 150 cc. of absolute alcohol and saturated with hydrochloric acid gas at 0°. In order to keep the alcohol constantly stirred, and at the same time exclude moisture, the delivery tube for the gas was provided on its lower end with a Witt stirrer, and the flask containing the nitril, as well as the gas exit from the hydrochloric acid generator, were provided with mercury seals constructed so as to keep moisture out of

[1] Ann. Chem. (Liebig), **303**, 80.
[2] *Ibid.*, p. 84.
[3] This method of preparation was worked out conjointly with S. F. Acree.
[4] Ann. Chem. (Liebig), **303**, 83.

the alcohol and allow a free rotation of the stirrer. Despite these precautions and the fact that after saturation the alcoholic solution was cooled to —25° for two hours, the imido ether did not separate out. After the solution had stood twenty-four hours the alcohol was distilled off *in vacuo* (bath at 60°), the residue taken up with a little water, and ammonia added to neutralization. The solution was now repeatedly shaken out with chloroform as long as any ester was obtained. The chloroform extracts yielded 24.7 grams of ester, or about 47 per cent of the theoretical. From the aqueous solution there separated out 2.8 grams of dihydromethyldioxy-α-triazine, or about 7 per cent of the theoretical. Sulphuric acid can be substituted for hydrochloric acid in the preparation of this ester, but thus far this method has not given so good a yield as does the hydrochloric acid method.

The Propyl Ester of Semicarbazinopropionic Acid.—This ester was prepared, similarly to the ethyl ester, by the action of propyl alcohol and hydrochloric acid on the nitril. Seven grams of nitril gave 3.5 grams of pure propyl ester. This ester is very soluble in alcohol and water, difficultly soluble in benzene, and very difficultly soluble in ether. It is best crystallized from benzene or acetic ether. From a solution of the latter it crystallizes, on evaporation, in long slender needles, which melt at 89° to a clear liquid.

0.2766 gram substance gave 0.4552 gram CO_2 and 0.2024 gram H_2O.

0.1586 gram substance gave 31 cc. N at 14° and 750 mm.

0.1598 gram substance gave 31.4 cc. N at 17° and 751 mm.

	Calculated for $C_7H_{13}O_3N_3$.	Found. I.	II.
C	44.44	44.88	....
H	7.95	8.13	....
N	22.22	22.69	22.53

The propyl ester, treated with potassium permanganate in dilute sulphuric acid solution, gives the corresponding ester of the semicarbazone of pyruvic acid,

$$NH_2CONHN = C(CH_3)COOC_3H_7,$$

a substance which separates out of very dilute solutions. It melts at 178° to a clear liquid.

0.1434 gram substance gave 27.9 cc. N at 17° and 756 mm.

	Calculated for $C_7H_{13}O_3N_3$.	Found.
N	22.47	22.46

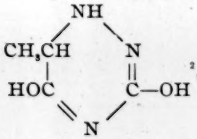
The Methyl Ester of Semicarbazinopropionic Acid.--Five grams of semicarbazinopropionic acid were allowed to stand four days with 120 cc. of a 3 per cent solution of hydrochloric acid in methyl alcohol. After neutralization with ammonium hydroxide the solution was evaporated to a small bulk and then extracted with chloroform. Yield 3.1 gram. No attempt was made to regain the unesterified acid. For the analysis the ester was crystallized from benzene, in which it is difficultly soluble, then from alcohol. From benzene it crystallizes in radiating bundles of slender prisms that melt at 100° to a clear liquid. With potassium permanganate in dilute sulphuric acid, the ester gives a semicarbazone which melts with decomposition at 208°.

0.1412 gram substance gave 34.4 cc. N at 27°.5 and 748 mm.

0.2377 gram substance gave 0.3248 gram CO_2 and 0.1476 gram H_2O.

	Calculated for $C_5H_{11}O_3N_3$.	Found.
C	37.27	37.27
H	6.83	6.90
N	26.09	26.31

Preparation of 3,5-Dioxy-6-methyl-1,6-dihydro-1,2,4-triazine,[1]



[2], from the ethyl ester of semicarbazinopropionic acid. The condensation of the ester to the triazine may be effected in four ways: (1) by the action of mineral

[1] It is not intended by this formula to distinguish between the several tautomeric possibilities.

[2] For the sake of brevity this substance will be referred to as triazine.

acids ;[1] (2) by heat ; (3) by alcoholic potash ; (4) by sodium alcoholate.

Two grams of the ester were heated for three hours at 120°. There was obtained from the fusion 0.5 gram of triazine, which was identified by its melting-point and solubilities.

To 10 grams of the ethyl ester in 25 cc. of methyl alcohol were added 12 cc. of a solution of caustic potash in absolute methyl alcohol. After three hours' standing, 5.4 grams of triazine had separated out. The filtrate, when neutralized with acetic acid, yielded 1.7 grams of triazine, making in all a yield equal to 83 per cent of the theoretical. As yet, semicarbazinopropionic acid has not been detected as one of the reaction-products here. The methyl and propyl esters are also converted into triazine by alcoholic potash.

If to 1 molecule of the ester, dissolved in the least amount of alcohol, there be added 1 molecule of sodium alcoholate in concentrated alcoholic solution, an immediate precipitation of the sodium salt of the triazine takes place. For the analysis the salt was filtered off, boiled with alcohol, washed with alcohol and finally with ether, and then dried for four hours at 110°. This triazine salt, unlike the corresponding salt of hydantoin, is very hygroscopic.

0.1656 gram substance gave 42.4 cc. N at 29° and 749 mm.

0.5150 gram substance gave 0.2362 gram Na_2SO_4.

	Calculated for $C_4H_6O_2N_3Na$.	Found.
N	27.81	27.56
Na	15.23	14.87

Five grams of the ester gave 3.28 grams of triazine, or about 89 per cent of the theoretical yield.

Action of Barium Hydroxide on the Triazine.—The triazine, on boiling with a barium hydroxide solution containing 2.4 grams of barium hydroxide to 1 gram of the triazine, for one-half hour, is changed into semicarbazinopropionic acid. One gram of triazine yielded 0.62 gram of pure acid, which proved identical with the acid obtained from semicarbazinopropionitril.

[1] Ann. Chem. (Liebig), **303**, 81.

0.2765 gram substance gave 68 cc. N at 13° and 751 mm.

	Calculated for $C_4H_5O_2N_3$.	Found.
N	28.57	28.72

3,5-Dioxy-6-methyl-1-benzoyl-1,6-dihydro-1,2,4-triazine—The ethyl ester of benzoylsemicarbazinopropionic acid,[1] treated in the usual way with sodium alcoholate, is converted into benzoyltriazine. The sodium salt does not separate out, but the benzoyltriazine can be isolated by the method given under lactylurea. It is readily soluble in hot alcohol, from which it crystallizes in short, microscopic prisms. This substance melts at 201° to a clear liquid, beginning to soften a few degrees below that point. After melting, it solidifies at about 180°, and then has a melting-point of 210°. This modification that melts at 210°, which is probably a tautomeric form, represents the labile form, as, on being crystallized from alcohol, it shows the same melting-point peculiarities as the original benzoyl derivative. Both before and after fusion the benzoyl triazine gives a deep reddish-brown color with an alcoholic solution of ferric chloride.

0.2436 gram substance gave 0.5057 gram CO_2 and 0.1052 gram H_2O.

	Calculated for $C_{11}H_{11}O_3N_3$.	Found.
C	56.65	56.62
H	4.72	4.80

The benzoyltriazine, on being heated with 10 per cent potassium hydroxide solution for a few minutes, is changed into 3-oxy-5-phenyltriazole-1-propionic acid, described by Bailey and Acree.[2] It showed the characteristic decomposition of the triazole at 240° to a deep-red liquid, and was further identified by a direct comparison with a sample of the triazole, prepared according to the method of Bailey and Acree, by a nitrogen determination, and by being converted into the ethyl ester of the triazole acid (melting-point 171° to 173°).[3]

The semicarbazone of the ethyl ester of pyruvic acid,

$$NH_2CONHN = C(CH_3)COOC_2H_5,$$

[1] Ber. d. chem. Ges., **33**, 1523.
[2] *Ibid.*, **33**, 1525.
[3] *Ibid.*, **33**, 1527.

does not undergo condensation with sodium alcoholate to form 3,5-dioxy-6-methyl-1,2,4-triazine,[1] as would be anticipated. Repeated experiments were carried out along this line, but in every case the unchanged semicarbazone was regained. The semicarbazone was also heated in the hope of effecting a triazine condensation in this way, but without success. Hydrochloric acid hydrolyzes the semicarbazone. The failure to prepare the triazine from the ester of semicarbazinopyruvic acid is to be regretted, as success in this direction would materially lessen the work in the study of this interesting compound. The semicarbazinopyruvic acid can be obtained almost quantitatively from semicarbazide hydrochloride and pyruvic acid, and the esterification of the semicarbazinopyruvic acid with a yield of over 95 per cent of the theoretical can be effected by boiling with a 3 per cent solution of hydrochloric acid in alcohol.[2]

Semicarbazinoisobutyric Acid, $NH_2CONHNHC(CH_3)_2COOH$.[3] — For the preparation of this substance semicarbazinobutyramide[4] in 25 times its weight of water is boiled with 0.5 molecule of barium hydroxide until the smell of ammonia disappears. The barium is then precipitated as sulphate, the water evaporated, and the acid crystallized from alcohol. Yield obtained, 55 per cent of the theoretical. The acid, as seen under the microscope, crystallizes in forms resembling cubes. It melts with decomposition at 194°. The acid is readily soluble in water and about 6 parts dissolve in 1,000 parts of alcohol at 25°.

0.1652 gram substance gave 40.6 cc. N at 30° and 746 mm.

0.2651 gram substance gave 0.3628 gram CO_2 and 0.1645 gram H_2O.

	Calculated for $C_4H_{11}O_3N_3$.	Found.
C	37.27	32.32
H	6.83	6.89
N	26.09	26.20

[1] Ann. Chem. (Liebig), **303**, 87.

[2] This esterification was worked out conjointly with C. P. Norby.

[3] The investigation of the butyric acid derivatives and the dimethyltriazine was carried out conjointly with M. B. Wesson.

[4] Ann. Chem. (Liebig), **283**, 36.

The Methyl Ester of Semicarbazinoisobutyric Acid, $NH_2CONHNHC(CH_3)_2COOCH_3$.—The acid is allowed to stand nine days with 25 times its weight of a 3 per cent solution of hydrochloric acid in methyl alcohol, and the ester then obtained in the usual way. Yield, 80 per cent of the theoretical. It is readily soluble in cold chloroform, alcohol, and water, and in hot benzene, and difficultly soluble in ether and petroleum ether. The ester crystallizes in bunches of long, slender, microscopic prisms, which melt at 106°.5, apparently undecomposed.

0.1514 gram substance gave 33.8 cc. N at 27° and 749 mm.
0.2063 gram substance gave 0.3110 gram CO_2 and 0.1385 gram H_2O.

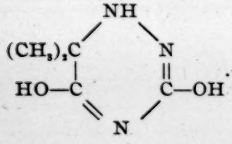
	Calculated for $C_6H_{13}O_3N_3$.	Found.
C	41.14	41.11
H	7.43	7.46
N	24.00	24.28

The Ethyl Ester of Semicarbazinoisobutyric Acid.—This ester was prepared similarly to the methyl ester and is about as soluble. It crystallizes from benzene in long, microscopic prisms, which melt at 97° to a clear liquid.

0.1517 gram substance gave 31.1 cc. N at 27° and 750 mm.

	Calculated for $C_7H_{15}O_3N_3$.	Found.
N	22.22	22.32

3,5-Dioxy-6-dimethyl-1,6-dihydro-1,2,4-triazine,



.—This triazine was prepared in the usual way from the ester and sodium alcoholate. The sodium salt of the triazine did not separate out of the alcoholic solution. The triazine is readily soluble in water, more difficultly soluble in alcohol, and crystallizes from the latter in thin plates with a silky luster. It melts at 230° to a clear liquid.

0.1741 gram substance gave 0.2683 gram CO_2 and 0.1007 gram H_2O.

	Calculated for $C_3H_9O_2N_3$.	Found.
C	41.96	42.03
H	6.29	6.43

Contributions from the Chemical Laboratory of the Massachusetts Institute of Technology.

XXXV.—THE ELECTROAFFINITY THEORY OF ABEGG AND BODLÄNDER.

By James Locke.

In reply to the recent article[1] in which Abegg and Bodländer have answered my criticism of their theory of electroaffinity as a basis for the systematization of inorganic compounds, I have little to say beyond adherence to the statements in my first article on the subject.[2] There are a few points, however, involving the question of careless interpretation or rendering of their theory on my part, which I should like to touch upon with brevity before allowing the subject to drop.

The main argument presented in my paper was that the three generic properties, sparing solubility, complex anion formation, and complex cation formation, or the reverse, ready solubility and the non-formation of complex ions, are not necessarily found correlated in the compounds of a given element. We sometimes see among the metallic salts a general sparing solubility without the formation of either complex anions or cations (Tl, Ba, etc.), sometimes difficult solubility and double salt formation without complex cations (Pb, Al, Fe^{III}, Au^{III}, Pt^{IV}, etc.), and sometimes the formation of both complex cations and anions, together with marked general solubility (Mg, Zn, Cd, Co, etc.). It seemed to me that this was a vital objection to their views, and that the assumption that such correlation does exist was not only embodied in their theory, but absolutely necessary to it if electro-

[1] This Journal, **28**, 220.

[2] *Ibid.*, **27**, 105.

affinity were to attain the dignity of a principle by which to classify all inorganic compounds.

My interpretation of their theory in this manner rested upon the fact that in their original paper[1] they devote several pages each to the following propositions:

1. That the solubility of the compounds of a given ion increases with the electroaffinity of the second ion until the electroaffinity becomes very great, in which latter case the effect is to decrease the solubility once more.

2. That the weaker the ions of a salt are (the less their respective electroaffinities), the greater becomes its tendency to form the "neutral constituent" of double salts.

3. That the lower the electroaffinity of an ion is, the more will the latter seek to strengthen itself by the addition of such a neutral constituent.

The neutral constituent may be either an ionizing compound, an element (oxygen, sulphur, etc.), or a non-electrolyte, such as ammonia or water. I have reread their first article very carefully, and find no indication of belief on the authors' part that the last two of these three properties are not directly commensurate with the electroaffinity. In the absence of a direct or indirect statement to the contrary, thereupon, it might naturally be taken for granted that these two properties are correlated with one another, and also with the degree of solubility (until "reverse solubility" results), since all three vary in the same direction with increasing electroaffinity. Abegg and Bodländer state in their present article, however, that in this respect I totally misunderstand their theory, and that the three properties need necessarily go together only when electroaffinity is responsible for the sparing solubility. They at the same time go to some length to explain that other influences come largely into play. In their first article such other influences were touched upon only once. The attempt was apparently made to trace the properties of all inorganic salts to the electroaffinities of their ions, and only in a single short paragraph, when they were forced to deal with the solubilities of such obstinate bodies as barium

[1] Ztschr. anorg. Chem., 20, 452.

sulphate, potassium platinichloride, and a few other salts, were outside causes for the behavior of these compounds even hinted at. If at the time of writing that article the authors did not consider the three properties as correlated, how can the following sentence from it (p. 457) be explained?

"But in these cases (instances in which the decomposition-voltage cannot be measured: L.), as will be shown below, the electroaffinity can be at least approximately estimated from the solubility and the tendency to form complex ions."

In case no correlation is assumed, why can either property alone be used as a criterion of the electroaffinity? On page 477 we find the solubility used to judge the electroaffinity of oxygen, and solubility and the formation of complex ions for that of sulphur. On page 493 the existence of only simple ions serves as an indication of the high electroaffinity of ammonium. Throughout the entire work one sees, by implication, that sometimes one property is made use of, again another; how arbitrarily may be shown by an attempt to derive the relative electroaffinities of lead, ferrous iron, and zinc from the degree to which they show the reactions involved. Lead salts are the least soluble, zinc salts form the most stable ammonia addition-products, and iron the most stable double salts. I doubt whether any system based upon such methods can ever become even an approximately useful means of classification. As is apparently recognized by Abegg and Bodländer in their second article, though not at all in their first, their basis of classification is completely hidden through the working of causes unknown, in all except the extreme members of the elements in their system. This being so, their proposition becomes one of adopting for all the elements offhand a system which is obviously applicable only to sodium, silver, and two or three other elements.

In this second paper, Abegg and Bodländer develop afresh their idea of reverse solubility—the decrease in solubility due to the presence in a salt of ions which have exceptionally high electroaffinities. Their remarks in this connection are so worded as to indicate that I had overlooked this point in their theory. I spoke of it as something without which the theory

in general could not stand for an instant. In their original article they state that owing to this reverse solubility effect "the salts of potassium, which has a higher electroaffinity than sodium, are in general less soluble than those of the latter." Here we have a concrete, hard and fast application of their theory to very soluble salts, emphasizing relatively very slight differences in solubility. They now state that "a single general law in the case of easily soluble compounds is not to be expected"—a direct tergiversation. That no such law can be applied in this particular case, and, therefore, that their original view of the relative solubilities of potassium and sodium salts is meaningless, is shown at once if we consider the compounds of more than two metals of high electroaffinity. Starting with zinc, the reverse solubility effect apparently becomes very great as we pass successively through the salts of calcium, strontium, and barium. Then, through lithium, it falls again until sodium is reached. In potassium it becomes stronger once more, only to sink away very noticeably in rubidium and, finally, caesium, which has the highest electroaffinity of all the metals. Caesium chloride dissolves in, at most, one-half its weight of water. I doubt whether, exclusive of the platinichloride, there is a single simple caesium salt which is less soluble than the corresponding potassium compounds. In my own experience with the metal, and this has been quite extensive, I have never found such a case. There is then, absolutely no regularity in the working of the reverse solubility effect, and the relative solubility of potassium and sodium compounds must be referred to some of the unknown causes which Abegg and Bodländer now bring forward to explain the numberless exceptions to their theory, instead of being regarded as a very striking confirmation of the latter.

According to statements in their original article, the authors regard basic salts as compounds of the anion X^- with the cation $M^{II}(OH)^+$. I mentioned the fact that, since according to this the metallic ion is "strengthened" by the addition of hydroxyl, a basic chloride should, by the theory, be more soluble than the normal chloride. Recognizing this sequence, they now suggest that the basic salt probably dis-

sociates in the sense $M^{II}X^{+}$ and $(OH)^{-}$, and support their view by the fact that basic salts are usually more soluble than the hydroxides. These two conceptions of the nature of a basic salt are far too fundamentally distinct and important to be slurred over lightly, and the passage from the one view to the other so suddenly by Abegg and Bodländer shows how arbitrarily one must proceed in order to make fact fit the theory.

Whether this particular change in view is of benefit may be doubted. Although the decomposition-voltage of hydroxyl is greater than that of chlorine, the authors assumed it, originally, to have a lower electroaffinity, probably to account for the fact that while chlorides are usually soluble, almost all hydroxides are insoluble. This assumption becomes, in fact, so very important that (p. 477) they regard tendency to hydrolysis as one of the best criteria of the electroaffinity of a metallic ion.

Adopting for basic salts the original formula, $M(OH)^{+}X^{-}$, this view is in accordance with their statements that when one of two ions enters into a complex it will be the weaker which does so (as in the compounds K^{+}, HSO_4^{-}, and H_2^{+}, $^{+}HgCl_4^{-}$, when K^{+} and H^{+}, Hg^{++} and H^{+}, are the ions in question). But this formula would require that basic salts be more soluble than normal salts. If we choose the other formula, still holding to the view that hydroxyl has a low electroaffinity, then the relative solubility of the hydroxide and basic salt is explained, but the above very pretty differentiation between acid salts and complex acids becomes meaningless. These two points can be reconciled only by the assumption of a high electroaffinity in hydroxyl—and this cannot be admitted because it would require hydroxides to be more soluble than chlorides. Whether the confusion here resulting is hopeless, or can be cleared up by research, remains to be seen. Until it is straightened out, however, electroaffinity can hardly be regarded as a suitable principle by which to systematize the mutual relations of bases, basic salts, normal salts, acid salts, and complex acids. And these occupy by no means inconsiderable space in the field of inorganic chemistry.

Abegg and Bodländer's pedagogical digression, in their last article, on the cause of the decreased solubility of thallous iodide when in the presence of an alkali iodide, is beside the mark. Noyes' work, which they rather captiously point out as if I had been ignorant of it, can be found cited in my article. They entirely pass over the real significance of such reactions of thallous thallium, of which I stated this to be a single example, and that is, that in spite of its low electroaffinity and the sparing solubility of its compounds the element has in the univalent state almost absolutely no tendency to enter into double salts. In their first article the low solubility here is directly ascribed to the low electroaffinity. In their second, as quoted above, they state that only when low solubility is directly due to low electroaffinity need the former be correlated with the formation of complex ions. The behavior of thallium, therefore, assumes some importance as an absolute exception even to the modified views which they now hold.

If a final confirmation is needed of my contention that in electroaffinity, Abegg and Bodländer are proposing, as a general principle of classification, a property which has been developed on, and can be applied to, only the most extreme members of the family of elements, it may be found in their last remark about the solubility of iodates and periodates. I had pointed out that if the ions of the latter are iodine strengthened by the addition of oxygen, then, by the theory, the salts should be more soluble than iodides. Abegg and Bodländer assume that I think the reader will have only the relations of the alkali salts in mind, and pointing out that here the phenomena are due to reverse solubility, they call attention to the fact that with metals which form typically insoluble iodides, the iodates and periodates are the more soluble of the three. I grant freely that this is so. On the one hand, we have sodium and potassium; on the other, silver, mercury, thallium, and possibly, but not probably, lead. But the alkaline earth metals, the earth metals, all the rare earth metals, iron and its trivalent analogues, magnesium, nickel, and their bivalent analogues, all the metals, in fact with electroaffinities between these extremes, in all their cathionic

forms, are they to be shut out from a general scheme of inorganic classification? The several periodates of all are obtained usually by precipitation. The iodates are almost all either insoluble or at least sparingly soluble. The iodides of all are probably even more soluble than the chlorides.

Here only two assumptions are possible. Either the authors have neglected to examine the literature, even after the contradictory behavior of the iodates and periodates had been pointed out to them, or they now wish to emphasize only the relation of electroaffinity to the properties of compounds of elements for which the latter is extremely high or low. This second assumption must, of course, be adopted. If it is true, then the authors' attitude is entirely different from that taken in their first article. There we find the properties of all the elements ascribed to their electroaffinity. Cupric amines, for instance, are more stable than cuprous, because the electroaffinity of the cupric ions is the less. The alkaline earth metals form no complex ions because of their high electroaffinity. Perchlorates, pyrosulphates, dichromates, are for the same reason more soluble than chlorides, sulphates, chromates; acid phosphates and acid carbonates than the normal salts. On page 474 we find a whole group treated at once. "Descending still further (from the alkali metals, alkaline earth metals, aluminium, and chromium, successively) in the series of decomposition-voltages, and therefore of electroaffinities, one comes to the heavy metals..... The complex compounds of iron, antimony, arsenic, copper, gold, and platinum, are prototypes of such bodies." Here there is certainly no attempt to limit the influence which electroaffinity is supposed to exert.

I hope to have shown in the above that since the publication of their first article, Abegg and Bodländer have very materially changed their attitude in regard to the general applicability of electroaffinity, at present at least, as a means of general classification. It is unfortunate that their answer to my criticism is so worded that this might not be understood by the more casual reader. Electroaffinity, as a property which stands in interesting and apparently very close relation

to the generic features of many salts, is a very different matter from "Electroaffinity: a new principle of chemical systematization." It ceases to be the latter, and becomes the former, as soon as the fact is recognized that in the great majority of cases its influence is almost entirely concealed by that of other, as yet, unknown causes. What the future of the theory may be must remain doubtful. But where its authors have attempted to analyze disturbing causes, in this last paper, as in discussing the irregularities in the formation of ammonia addition-products, one can hardly call their efforts successful. The only causes isolated as yet are such as, according to their first paper, should themselves act with an intensity dependent directly upon the electroaffinity, and which, therefore, should produce no irregularity whatever, but rather bring about still sharper gradation.

BOSTON, MASS., Sept. 15, 1902.

REVIEWS.

INDICATORS AND TEST-PAPERS: THEIR SOURCE, PREPARATION, APPLICATION, AND TESTS FOR SENSITIVENESS. By ALFRED I. COHN, PH.G. Second edition, revised and enlarged. New York: John Wiley & Sons. 1902. Price, $2.00.

The reception which the first edition of this book was accorded has led to the preparation of a second edition in which the recent developments in the line of indicators have been incorporated. It is a very valuable reference book for all who have to deal with the use of indicators or test-papers, and should be readily accessible to every chemist. J. E. G.